VOL. XXXIX. FEBRUARY, 1908. NO. 2.

.39
908

AMERICAN

CHEMICAL JOURNAL

SOME EFFECTS OF SUNLIGHT UPON COLORLESS GLASS.

BY ROSS AIKEN GORTNER.

Within recent years, a number of instances have been reported, from various parts of the world, concerning the violet coloration of glass when exposed to the sunlight.[1]

Fischer[2] has induced the same change in colorless glass, containing a comparatively small proportion of manganese, by exposure to the rays of a mercury lamp, thus showing that the change is due to the ultraviolet rays.

Up to the present time only one instance, which was observed by the writer,[3] has been reported indicating the time of exposure actually required to produce the change in the color of the glass.

On July 9, 1906, twenty-two specimens of glass were firmly fastened to a board by means of aluminium wire and the board exposed upon the slate roof of a building at Lincoln in a position facing the south and inclined at an angle of about 45°.

[1] Crookes: Chem. News, **91**, 73 (1905). Avery: J. Am. Chem. Soc., **27**, 909 (1905). Simpson: Chem. News, **91**, 236 (1905). Rueger: J. Am. Chem. Soc., **27**, 1206 (1905). Alway and Gortner: THIS JOURNAL, **37**, 1 (1907).

[2] Ber. d. chem. Ges., **38**, 946 (1905).

[3] THIS JOURNAL, **37**, 1 (1907).

The spot selected was about 75 feet above the ground and was exposed to the direct rays of the sun for the entire day excepting, perhaps, in June and July for an hour before sunset when a low tower on the west cast a shadow on the board. The specimens, when on the building, were at an elevation of about 1200 feet above sea level.

Specimens 1 to 12, inclusive, were rectangular 4-ounce bottles of the same make and were obtained from a local dealer. They were exposed, filled with various substances, numbers 1 to 6 being filled with chalk colored, respectively, with picric acid, indigo, methyl violet, "wasserblau," malachite green, and sodium eosin. Number 7 was filled with manganese dioxide, number 8 with lampblack, number 9 with sodium eosin solution, number 10 with potassium permanganate crystals, number 11 with chalk, while number 12 was exposed empty. Numbers 7, 8, and 10 were filled with their respective contents in order to determine what truth there might be in the theory of Chas. Rueger[1] that glass might become "violet by lying for some time in the proximity of bodies heavily charged with manganese." Number 13 was a bottle of a different make and was exposed filled with potassium chromate crystals. Number 14 was the base of a broken goblet which was found upon the street and which, as yet, showed no trace of violet coloration although it might have been exposed to the sunlight for some time. Number 15 was a small glass funnel, number 16 a small round solution bottle, number 17 a 50 cc. Erlenmeyer flask of Jena glass, number 18 an ordinary round 50 cc. flask, number 19 a small homeopathic vial of American manufacture, number 20 a piece of hard glass tubing, and numbers 21 and 22 pieces of soft glass tubing. Numbers 15, 16, 17, 20, 21, and 22, were secured from the "Vereinigte Fabriken," Berlin.

One month after exposure the specimens were examined and it was found that numbers 13, 14, 21, and 22 had become slightly violet, number 13 being of so decided a violet tinge that the coloration was noticeable several feet away.

The specimens of glass then remained undisturbed until the 21st of March, 1907, when they were again examined. At

[1] J. Am. Chem. Soc., **27**, 1206 (1905).

that time they all showed some violet coloration excepting numbers 15, 16, 17, and 20, which still remained colorless. Numbers 13 and 21 had, by this time, become intensely violet. Number 22 could not be found, evidently having been blown away by the wind.

On May 31, 1907, the board was removed from the roof and the bottles, after being cleaned, were given a close inspection, with the following result: number 1 was distinctly violet on the upper face, less violet on the sides, but still enough so that the coloration was plainly visible, and almost colorless on the back. Numbers 2, 4, 5, 6, and 11 differed in no way from number 1. Number 3, which had contained chalk colored with methyl violet, was of a deeper color on the upper face and sides and was also of a faint violet on the back. Number 7 (filled with manganese dioxide) and number 8 (filled with lampblack) were indistinguishable from each other, being less violet on the surface and sides than the preceding numbers and showing almost no color on the back. Number 9 had been broken by the freezing of its contents; the violet tinge on the face and sides was pronounced, and on the back, less so. No 10, containing potassium permanganate crystals, was the least colored of the series 1–12, being slightly less violet than numbers 7 and 8. There was a faint violet tinge upon the upper face and almost no color whatever upon the sides and back. Number 12, being empty, was of a uniform violet throughout and the color could not be distinguished from that of the face of number 1. Number 13 was a very intense violet upon the face and sides and of a deep violet on the back. This is the best specimen of violet colored glass that I have been able to secure in Nebraska, although it is surpassed in intensity of coloration by some specimens from the steppes of Canada and from New Mexico.[1] Number 14 was of a deep violet throughout, being more intense in color than number 12 and much less intense than number 13. The shade was slightly deeper than on the back of number 13. Numbers 15, 16, 17, and 20 showed no trace of violet coloration. Numbers 15, 16, and 20, as will be shown later in the table of analyses, contained no manganese, and number 17, although

[1] The specimens from New Mexico were secured from Dr. Avery.

containing manganese, was not colored violet by the action of the sunlight. An explanation for this may be found in the composition of Jena glass which may prevent the necessary chemical change from taking place. Fischer[1] met with similar results when Jena glass was exposed to the rays from a mercury lamp. Numbers 18 and 19 were distinctly violet throughout. Number 21 was distinctly violet when seen from the side, even at a distance of several feet, and when viewed lengthwise, the violet coloration was very intense, being but a shade lighter than number 13.

In order to obtain the manganese content, the method of H. Noll[2] was employed. Portions of the specimens were ground to a powder, fused with sodium and potassium carbonates, dissolved in dilute hydrochloric acid, precipitated with ammonia and bromine water, and allowed to stand for 12 hours. The precipitate was then filtered out, washed, and treated with 1 gram potassium iodide and 4 cc. concentrated hydrochloric acid. After standing for five minutes the iodine set free was titrated with N/100 sodium thiosulphate. From the iodine set free the manganese is calculated.

The color of the beads which were obtained by the fusion ranged from a deep purple in number 13 to colorless in numbers 15, 16, and 20. The range of coloration was in the following order: 13, 11, 19, 18, 21, 14, and 17, 13 being the most colored and 17 the least. The beads obtained from numbers 1 to 12 were indistinguishable and therefore number 11 was selected to represent the series.

The accompanying table gives the percentage of manganese and shows the relation of this to the change in color on the face of the specimen. "Slight" means slightly violet, "pale" means pale violet, etc.

The influence of the exposure of glass is well illustrated by the color of the basement windows of a church near Lincoln which has been built for five years. The windows are of pressed glass, and on the south and west sides are of such a distinctly violet color as to be easily noticeable a hundred yards away,

[1] Ber. d. chem. Ges., **38**, 946 (1905).
[2] Centrabl., 1907, 1 1223 (Apr. 17).

No. of sample.	Description of sample.	Per cent of manganese.	Color after 1 month.	Color after 8 months.	Color after 11 months.
15	small funnel (Verein. Fabrik.)	0.000	none	none	none
16	100 cc. bottle (Verein. Fabrik.)	0.000	"	"	"
20	hard glass tubing (Verein. Fabrik.)	0.000	"	"	"
14	base of goblet	0.049	slight	distinct	deep
17	50 cc. Erlenmeyer flask (Jena glass)	0.072	none	none	none
1	bottle with chalk colored with picric acid		"	light	distinct
2	" " " " " indigo		"	"	"
3	" " " " " methyl violet		"	distinct	"
					deeper than No. 1
4	" " " " " "wasserblau"		"	light	distinct
5	" " " " " malachite gr'n		"	"	"
6	" " " " " sodium eosin	0.075	"	"	"
7	" " manganese dioxide	to	"	pale	light
8	" " lampblack	0.087	"	"	"
9	" " sodium eosin solution		"	distinct (broken)	distinct
10	" " potassium permanganate crystals		"	faint	very light
11	" " chalk		"	distinct	distinct
12	" empty		"	"	"
19	homeopathic vial (American manufacture)	0.14	"	"	deep
18	round flask (American 50 cc.)	0.17	"	"	"
21	soft glass tubing	0.20	pale	"	"
13	bottled with potassium chromate crystals	0.34	distinct	deep	very deep
22	soft glass tubing	(?)	"	lost	lost

.39
908

while on the north and east sides there is almost no coloration. When closely examined, the violet coloration is so intense as to be comparable only to the deeper-colored glass found on the high plains of Canada. The coloration is as deep as that of number 13 although the manganese content is only 0.126 per cent, the deep color being probably due to the length of exposure.

Beside the specimens of violet-colored glass secured in this vicinity, the writer has found many scattered over eastern and northern Nebraska and has received some from the second steppe of Canada. The latter came from southern Saskatchewan at an elevation of about 2000 feet.

Summary.

Glass containing a relatively large percentage of manganese may show a violet coloration when exposed to sunlight for a period of less than a month, the degree of coloration being proportional to the manganese content.

Exposure of less than a year will produce a violet coloration in most glasses containing only a small percentage of manganese, but this coloration will become more pronounced when the time of exposure is increased.

Should a glass be colored violet by the action of sunlight, proof is furnished that the glass contains manganese. However, not all glasses containing manganese are colored violet by exposure to sunlight, as is shown by the Jena Erlenmeyer.

A background or subsoil containing manganese or ores of manganese will have no influence upon the coloration of glass lying upon it.

A violet background is more favorable to the action of the ultraviolet rays than other colors: white, yellow, blue, and red act alike and seem to have no effect, while brown and black seem to have a retarding effect.

LINCOLN, NEBRASKA,
August 1, 1907.

STUDIES ON SOME SOILS FROM SASKATCHEWAN.

By Leverne L. Clark, Ross A. Gortner, and Carey E. Vail.

Hilgard[1] has pointed out that, while the fine soil particles (grains of a diameter of less than 0.025 mm.) under humid conditions contain almost the whole of the available plant food of the soil, it is different in regions of deficient rainfall. In the latter "much actual plant food may be present in rather coarse sandy soils, almost devoid of clay; such as in humid climates would be likely to be found wholly barren."[2] This is well illustrated by the work of Loughridge[3] on a generalized soil of the state of Mississippi and also on sandy and adobe soils of California. Later investigations by Rudzinski[4] and by Mazurenko[5] on loess and podzol soils from European Russia corroborate the work of Loughridge.

The analyses reported in this article are those of a boulder clay from southern Saskatchewan.[6] All of the samples are from the region of treeless plains, characterized by a low rainfall which occurs almost exclusively during the growing season. Seepage on the heavier soils probably does not occur to any appreciable extent. The mechanical analysis of a sample of boulder clay was made with the following results:

	Per cent.
Gravel, 2.0 to 1.00 mm.	1.7
Coarse sand, 1.0 to 0.5 mm.	5.2
Medium sand, 0.5 to 0.25 mm.	5.6
Fine sand, 0.25 to 0.10 mm.	14.1
Very fine sand, 0.10 to 0.05 mm.	12.3
Coarse silt, 0.05 to 0.016 mm.	16.2
Fine silt, 0.016 to 0.005 mm.	19.5
Clay, 0.005 to ?	26.1
Total	100.7

[1] Hilgard: Soils, pp. 87 and 386.

[2] *Ibid.*, p. 88.

[3] Report, Agr. Exp. Sta., Univ. of Cal., 1898–1901, Part 1, p. 33.

[4] Exp. Sta. Record, **16**, 345 (1904–05). Izv. Moscow Selsk. Khoz. Inst. (Ann. Inst. Agron. Moscow), **9** (1903), No. 2, pp. 172–234, pls. 5.

[5] Exp. Sta. Record, **16**, 344 (1904–05). Inaug. Diss., Munich; abs. in Zhur. Opuitn. Agron. Jour. Expt. Landw., **5** (1904), 1, pp. 73–75.

[6] Alway: This Journal, **36**, 580 (1906). Alway and McDole: *Ibid.*, **37**, 275 (1907).

The Vertical Distribution of Soluble Salts in the Soil.

A known weight of air-dried soil of each foot section was treated with a known volume of distilled water and allowed to stand with frequent shaking for 72 hours. The soil was then allowed to settle and the supernatant liquid siphoned off and filtered through double "barium" filters. An aliquot portion was then evaporated to dryness on a water bath in a platinum dish and dried to constant weight at 100°. The following were the percentages of soluble salts found in five different bores.

No. of bore.	1.	2.	3.	4.	5.
1st foot	.40	.27	.16	.28	.26
2nd foot	.26	missing	.12	.22	.15
3d foot	.15	.15	.11	.12	.05
4th foot	.07	.10	.10	.09	.06
5th foot	.05	.08	.06	.08	.04
6th foot	.06	.09	.07	.19	.05
Average	.16	.14	.10	.17	.10

The Composition of the Water-Soluble Portion of the Soil.

Equal quantities of each foot section of air-dried soil were mixed and treated with a known volume of water. After standing, with frequent stirring, for 72 hours, the supernatant liquid was siphoned off and filtered. A portion was evaporated to dryness in a platinum dish and dried to constant weight at 100° in order to ascertain the total alkali present. The remainder was analyzed with the following results:

	Per cent.
Na	14.18
K	1.75
Mg	11.04
Ca	2.79
SO_4	47.45
Cl	10.84
CO_3	3.42
H_2O (by difference)	7.53
Total	100.00

Chemical Composition of the Soil Particles of the Different Sizes.

The beaker method of separation was used, the soil being first boiled with distilled water until it was in a fine state of division, each grain being separate from the others. Equal portions of each foot section were mixed and, after boiling, separated by means of decantations from beakers into the various-sized grains. The clay which remained suspended in the water was precipitated by means of ammonium chloride, the clear liquid siphoned off, and the precipitated clay dried and powdered. The high percentage of volatile matter found in the clay is due partly to the presence of ammonium chloride. Particles of from 1.0 to 0.05 mm. in diameter are classified as sand, from 0.05 to 0.016 mm. as coarse silt, from 0.016 to 0.05 mm. as fine silt, and smaller than 0.005 mm. as clay.

Hilgard's method[1] was used in the chemical analysis of the separated portions. The following results were obtained from the four portions into which the soil was separated:

	Sand.		Coarse silt.		Fine silt.		Clay.
Insoluble matter	82.85	85.03	59.05	64.86	31.95	53.63	15.24	43.51
Soluble silica	2.18		5.81		21.68		28.27	
CaO		4.93		10.29		9.36		0.84
FeO_3		1.54		2.19		5.74		8.59
Al_2O_3		0.60		1.74		7.50		11.87
Mn_2O_7		0.07		0.25		0.14		0.16
MgO		1.40		4.79		3.57		2.23
Na_2O		0.14		1.04		.82		1.12
K_2O		0.11		.58		1.52		2.08
CO_2		4.59		12.42		8.87		0.29
SO_3		0.06		0.15		0.07		0.07
P_2O_5		0.10		0.22		0.22		0.30
Volatile matter		0.37		2.76		7.83		28.63
Total		98.94		101.29		99.27		99.69

LINCOLN, NEBRASKA,
August 10, 1907.

[1] Circular No. 6, Agricultural Exp. Station, University of California.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

STUDIES IN CATALYSIS. II. THE CATALYSIS OF IMIDOESTERS.

By Julius Stieglitz.

In the first paper,[1] it was stated that an imidoester is decomposed by water in two ways,

$$RC(:NH)OR' + H_2O \rightarrow RCOOR' + NH_3 \qquad (1),$$

and

$$RC(:NH)OR' \rightarrow RC \vdots N + HOR' \qquad (2).$$

The first action, which can just be detected and measured in aqueous solutions,[2] is accelerated enormously by the addition of acids, and it was shown in the first report that the acceleration is proportionate to the salt formed. Since dilute solutions, in which the imidoester salts are very largely ionized, were used, the conclusion was drawn that the reacting component for expression (1) is really the positive imidoester ion, which is decomposed by water thus:

$$RC(:\overset{+}{N}H_2)OR' + HOH \rightarrow RCOOR' + \overset{+}{N}H_4 \qquad (3).$$

This conclusion is borne out by Schlesinger's determinations[3] of velocities with more concentrated solutions of the imidoester salts, for which the degrees of ionization were also determined. These results will be briefly discussed below in Part VIII.

The second of the above reactions is accelerated enormously by the addition of alkalis. This fact is particularly interesting, as it draws still closer the parallelism between ordinary esters and the imidoesters. According to our theory of catalysis, the acceleration by the alkalis or, rather, their hydroxyl ions, would be due, by analogy to the action of acids, to salt formation between the alkalis and the imidoesters, from which the possession of weak acid properties and, consequently, of

[1] This Journal, **39**, 29 (1908).

[2] *Vide* a later paper by Miss Barnard.

[3] *Vide* a later paper by H. I. Schlesinger.

an amphoteric character must follow. The application of our theory to this case will be considered below in Part VI.

The reacting component, then, for expression (2) is again not the imidoester itself, but rather its negative ion, the velocities having been found proportionate to the concentration of this ion. We have

$$RC(:\overline{N})OR' \rightarrow RC \vdots N + \overline{O}R \qquad (4).$$

Besides these two reactions, we have still a third one, the study of which has been particularly interesting: in purely aqueous solutions, when neither acid nor added alkali is present, we also have a decomposition of the imidoester into nitrile and alcohol according to expression (2), and the reacting component in this case is the *nonionized* or molecular imidoester. This action is very much slower than either of the ion reactions under the influence of acids or bases. This possibility was considered and examined carefully: whether the imidoester being a base and rendering the solution distinctly alkaline, the decomposition in aqueous solution might not represent a case of autocatalysis, proceeding really according to expression (4) under the influence of its own hydroxyl ions, rather than a third reaction of the imidoesters. But from a rigorous analysis of the case, the conclusion must be drawn that the velocity in aqueous solution is chiefly due to a slow decomposition of the nonionized substance according to (2), the velocity being found much greater than could be accounted for by the amphoteric properties of the imidoesters. The action will be discussed in detail in Part VII.

As giving an insight into the nature of the reactions of organic compounds (and the same considerations apply equally to inorganic compounds), it is considered extremely interesting to have thus found that the imidoesters react by means of three components, each reacting with characteristic velocity constants: their positive ions forming, with water, acid esters and ammonium ions; their negative ions forming nitriles; and the nonionized molecules forming nitriles and alcohols also, but with their own characteristic velocity constant. It is particularly noteworthy that the reaction velocities of

the ion forms are very much greater than those of the non-ionized molecules.

Schlesinger's determinations of the velocities of decomposition of the imidoester salts in more concentrated solutions led to the recognition of a *salt effect* or *salt catalysis*, influencing the velocity of decomposition of the imidoesters by water, just as there is a salt catalysis of ordinary esters, cane sugar, etc. Similar effects were then recognized in experiments carried out with Derby[1] and McCracken[2] on the speeds of reaction of imidoesters in the presence of an added excess of hydrochloric acid. Rough determinations of the order of this salt acceleration have been made and have suggested a very interesting conclusion, but as a very thorough investigation of this part of the problem has been made by Miss Barnard,[3] giving a better foundation for our conclusions, a brief discussion of our earlier results in Part VIII will be sufficient.

In the first paper attention was called to the conclusion that there is a tendency, under the influence of acids, toward a decomposition resulting in the formation of the ion of a stronger base from the positive ion of a weaker base—the ions of the imidoesters, for instance, the weaker bases, forming ammonium ions, the ions of a much stronger base. An investigation of the question whether the reaction velocities are greater, the greater the difference in the affinity constants of the two bases, was carried out by Mr. McCracken and will be discussed in Part IX.

In this tendency, studied experimentally and quantitatively for the imidoesters, we have still another analogy between the imidoesters and ordinary esters,[4] and as the substitution of imidoesters, for which we have been able to determine experimentally all the constants and factors involved in our calculations, for ordinary esters in the experimental study of the theory of catalysis forms a vital step in our study, the

[1] *Vide* a later paper by Ira Derby.
[2] *Vide* a later paper by W. McCracken.
[3] *Loc. cit.*
[4] Euler: Z. physik. Chem., **38**, 419 (1901).

parallelism between the two classes of esters, as it now appears as the results of our work, will be summarized in Part X.[1]

VI.[2] *The Catalysis of Imidoesters in Alkaline Solutions.*

That imidoesters, RC(: NH)OR′, should have weak acid properties, besides being pronounced bases, is not surprising in view of the fact that the very much stronger, closely related bases, the amidines, have the power to form salts with metals, as has been known for some time. Thus, phenylmethylisourea, $C_6H_5NHC(:NH)OCH_3$, which is at the same time an amidine and an imidoester, forms a silver salt, $(C_6H_5)NHC(:NAg)OCH_3$.[3] Carbamide itself, as is well known, forms a disilver salt, to which the structure $NH_2C(:NAg)OAg$ must be assigned. The substitution of a negative group, such as C_6H_5, $NO_2C_6H_4$, for the positive amide group, NH_2, must strengthen the acid tendencies of the molecule, although it still remains an exceedingly weak acid, as is hydrocyanic acid, C: NH,[4] which may be considered the prototype of all these acids.

For an exceedingly weak acid,

$$RC(:NH)OR' \rightleftharpoons RC(:\overset{-}{N})OR' + \overset{+}{H} \qquad (4),$$

for which we have,

$$C_{neg.ion} \times C_H = k_{aff.} \times C_{mol.} \qquad (5).$$

We may put the molecular concentration equal to the total concentration of the ester, the ionized part being negligible in calculating $C_{mol.}$, and taking the ionization of water into account, we have

$$C_{neg.ion} = k_{aff.} \times \frac{C_{ester}}{C_H} \qquad (6),$$

$$= \frac{k_{aff.}}{k_{HOH}} \times C_{ester} \times C_{OH} \qquad (7).$$

[1] Later papers will take up in detail the question of the catalytic actions of the imido- and ureaesters with ammonia and ammonium chloride, and the question of the "salt effect". The investigations, carried out by Miss Edith Barnard, Miss Katharine Blunt, and Mr. R. A. Hall, have already been completed.

[2] Parts I. to V. are in the first report, THIS JOURNAL, **30**, 29 (1908).

[3] Stieglitz and Bruce: J. Am. Chem. Soc., **26**, 435 (1904).

[4] $K_{HCN} = 1.3 \times 10^{-9}$. Ammonia unquestionably ionizes to a very slight degree into $\overset{+}{H}$ and $\overset{-}{NH_2}$; the metal amides are derived from the $\overset{-}{NH_2}$ ions and the reactions of ammonia in which it is absorbed must be due to these ions.

For a reaction

$$RC(:\bar{N})OR' \rightarrow RCN + \bar{O}R' \qquad (2),$$

in which the negative ion is the reacting component, we have[1]

$$\frac{dx}{dt} = k_v \times C_{neg.ion} \qquad (8).$$

By substituting into equation (8) the value found for $C_{neg.ion}$ in equation (7), we obtain

$$\frac{dx}{dt} = k_v \times \frac{k_{aff.}}{k_{HOH}} \times C_{ester} \times C_{OH}$$

$$= K_v \times C_{ester} \times C_{OH} \qquad (9).$$

For an exceedingly weak acid then, whose negative ions are decomposing according to (2), we should find the velocity of the decomposition proportionate to the total concentration of the ester and to the concentration of the hydroxyl ion.[2]

Dr. Schlesinger, using this equation, obtained excellent constants for five imidoesters (methyl, ethyl, propyl, isopropyl imidobenzoate and methyl imido-*m*-nitrobenzoate). Even for the most stable (slowest reacting) imidoester, isopropyl imidobenzoate, the velocity constant was a very high one, $K_v = 0.265$ at 25°, and for the nitro ester the constant was 3.66. These constants are very much larger than those for the velocities of decomposition in acid solutions (see the first report). And so the imidoesters resemble the esters also in being decomposed much more rapidly by alkalis than by acids.

VII. The Decomposition of Imidoesters in Aqueous Solutions.

The decomposition of an imidoester in aqueous solution into an alcohol and a nitrile (expression 2) may be the result of three different causes:

(1) The substance actually undergoing the decomposition might be the nonionized base. As the imidoesters are ex-

[1] $C_{neg.ion}$ is a function of x.

[2] Equations (8) and (9) are the fundamental equations for reactions—so-called catalytic—accelerated by alkalis. They correspond to the equations given in Vol. IV, p. 281, Congress of Arts and Science, St. Louis, 1904, and in the first paper [THIS JOURNAL, **39**, 29 (1908)] for reactions accelerated by acids.

ceedingly weak bases and are hardly ionized at all, the reaction velocity must then be proportionate to the total concentration of the esters, and we have a reaction of the first order,

$$\frac{dx}{dt} = K_{mol.} \times (C - x) \qquad (10),^{1}$$

and

$$K_{mol.} = \frac{1}{t_2 - t_1} \log \text{nat} \frac{C - x_1}{C - x_2} \qquad (11).$$

As is shown in the tables given below, excellent constants are obtained when the reaction velocities are calculated according to this equation.[2]

(2) The reacting component may be the negative ion of the imidoester. Schlesinger having found that hydroxyl ions accelerate the decomposition into nitrile and alcohol, and these being the chief products of decomposition also in aqueous solution, it could very well be that in the aqueous solution *the hydroxyl ions of the base itself* cause the decomposition by the formation of more negative imidoester ions—by a kind of autocatalysis.

For this action we have the velocity of the reaction given by the equation

$$\frac{dx}{dt} = K_{neg.ion} \times C_{ester} \times C_{OH} \qquad (9).^{3}$$

If the decomposition of the imidoester by water is primarily due to the negative ions and the hydroxyl ions, as expressed in this equation, then, the imidoesters being weak bases and at the same time weak acids (amphoteric), the concentration of the hydroxyl ions would be a variable dependent at every moment on the concentration of the free base. If salt formation occurs to any but a negligible extent, the concentration of the hydroxyl ions formed from the base would be very largely affected by the increased concentration of the positive

[1] $C - x$ represents the concentration of the ester at any moment t.

[2] From what follows, it will become apparent that the mere fact that a very good constant was obtained according to (10) and (11) would not warrant one in proceeding no further in the analysis of the action—a second equally good constant might appear by another interpretation (see below).

[3] *Vide VI.*

ions as a result of salt formation. The ionization constant of the ester as an acid is so small that we have not yet attempted to determine it and we have deemed it sufficient to consider the two extreme possibilities of the case. The first —the imidoesters being such strong bases that their solutions react decidedly alkaline—is that the acid character may be considered so weak as not to affect the value of the hydroxyl concentration by the production of a salt and its positive ions. This assumption leads to a *maximum* possible value for the concentration of hydroxyl ions and this restriction is quite sufficient for the purpose of this discussion. The second extreme assumption is that the positive and negative ions are formed *chiefly from the salt* produced by the amphoteric character of the esters. Under (2A) the first extreme assumption will be treated, under (2B) the second one.

(2A) For a weak base we have

$$C_{pos.ion} \times C_{OH} = k_{aff.} \times C_{mol.} \qquad (12),$$

and if salt formation can be neglected,

$$C_{pos.ion} = C_{OH} \qquad (13).$$

We may also put, as a very close approximation,

$$C_{mol.} = C_{ester} \qquad (14).$$

Then, from (12), (13), and (14), we have at any moment,

$$C_{OH} = \sqrt{k_{aff.} \times (C-x)} \qquad (15),$$

in which (C—x) represents the concentration of the imidoester at any moment. C_{OH} will represent, then, a *maximum* concentration of hydroxyl ions, according to the assumption made.

Substituting the values for C_{OH} and for C_{ester} in equation (9), representing the velocity of the reaction, we have

$$\frac{dx}{dt} = K_{neg.ion} \times \sqrt{k_{aff.} \times (C-x)} \times (C-x) \qquad (16),$$

and

$$t = \frac{1}{K_{neg.ion.} \sqrt{k_{aff.}}} \int \frac{dx}{(C-x) \times \sqrt{C-x}} \qquad (17).$$

Integrating, we find

$$K_{neg.ion} = \frac{2}{t \times \sqrt{k_{aff.}}} \left(\sqrt{\frac{1}{C - x_t}} - \sqrt{\frac{1}{C}} \right) \qquad (18).$$

Or, if we express the concentrations in terms of parts of 1 gram molecule of ester in V liters,[1] and if v_o and v_t cc. standard acid are used to neutralize a given volume of solution at the moments $t = 0$ and $t = t$, we have simply

$$K_{neg.ion} = \frac{2}{t} \sqrt{\frac{V}{k_{aff.}}} \left[\sqrt{\frac{v_o}{v_t}} - 1 \right].$$

While fairly good constants were obtained according to this equation for single experiments, the values obtained with different concentrations of the base did not agree with each other. At the same time, the values thus calculated for $K_{neg.ion}$ are *very much higher* than the same constant as determined rigorously for the decomposition of the imidoesters in alkaline solutions.[2] For instance, for methyl imidobenzoate, catalyzed in the presence of barium hydroxide, $K_{neg.ion}$ is found by Schlesinger to be 1.97, but, as shown in the tables given below, if the reaction were an autocatalytic effect of the hydroxyl ion of the imidoester, in aqueous solution the constant would range between 20 and 40. The determinations for the other imidoesters show similar differences.

In other words, the velocity of decomposition in aqueous solutions is far too great to be accounted for by the decomposition of the negative ion by a process of autocatalysis, analogous to the catalysis by alkalis as discussed in Part VI., although we have assumed a maximum possible concentration of the hydroxyl ion. Consequently this interpretation of the action must be rejected.

(2B) On the basis of the second extreme assumption for the condition of an imidoester in aqueous solution, *viz.*, that its ionization is chiefly due to its amphoteric character and the ionization of the salt obtained from the acid and the basic forms, we have, according to Arrhenius, just as for aniline acetate,

[1] $C = 1/V$.

[2] Page 169.

$$\frac{C_{neg.ion} \times C_{pos.ion}}{C^2_{ester}} = \frac{k_{acid} \times k_{base}}{k_{HOH}} = K \qquad (20).^1$$

In accordance with the assumption made that the ions are derived chiefly from the salt, we may put

$$C_{neg.ion} = C_{pos.ion},$$

and have then

$$\frac{C^2_{neg.ion}}{C^2_{ester}} = K,$$

or

$$C_{neg.ion} = \sqrt{K} \times C_{ester} = K' \times C_{ester} \qquad (21).$$

In other words, for an amphoteric substance, such as this, if the reaction velocity is found proportionate to the total nonionized substance, C_{ester}, as expressed in equation (10) and as is actually found by experiment (see below), a constant would also result by putting the reaction velocity proportionate to the concentration of the negative ions (or the positive ions) as the reacting substance, since, according to (21), the concentration of the ions is proportionate to that of the molecular substance (C_{ester}).

To decide between the two possibilities, with each of which the experimental data for purely aqueous solutions, considered alone, would agree, one need only compare the velocity constant for the negative ions of the amphoteric substance as found in aqueous solution with that found in solutions containing a known amount of alkali (hydroxyl ions). As was explained above, the speed of decomposition in aqueous solution is far too great to be accounted for by salt formation of the amphoter, even when the maximum value for C_{OH} and, consequently, the *maximum* value for the negative ions is assumed.[2] Consequently, although a *constant* would be obtained on the basis of this second extreme assumption (2B), that the ions come chiefly from the salt formation between the acid and the basic parts, it would agree even less with the other facts determined for the decomposition than did the as-

[1] The amount ionized is considered negligible.

[2] $C_{neg.ions} = C_{ester} \times C_{OH} \times k.$ (7).

sumption made in (2A), and it must be rejected as not representing the main reaction under investigation.[1]

(3) The third theoretical possibility is that the reacting component in the decomposition of an imidoester in purely aqueous solution is neither the nonionized molecule nor its negative ion, but rather the positive ion of the amphoter. This possibility can be disposed of at once by the fact that the decomposition products of the positive ions in the presence of water have been shown to be an ester and ammonium ions; in the case under discussion, the chief products are the nitrile and an alcohol, and only traces of ester and ammonia are formed. The decomposition velocity cannot be due to the positive ion.

In the following tables two or three illustrative results are presented. The time is given in minutes in the first column. In the second column the volume of N/10 acid used to neutralize a given volume w of the base solution at any moment t is given. Column three gives the velocity constant calculated according to equation (11), the velocity being put proportionate to the total molecular concentration of the imidoester; and in the last column we have the constant calculated according to equation (19) as a reaction of the negative ions, accelerated autocatalytically by the alkaline properties of the imidoesters.

Table I.[2]*—Methyl Imidobenzoate at 25°.*

N/20. w = 25 cc.

t.	v_t.	$4343\,K_{mol.}$	$K_{neg.ion.}$
0	12.49	....	....
60	12.27	1.28	19.6
200	11.85	1.15	16.8
260	11.70	1.09	....
400	11.28	1.11	16.7
1340	8.66	1.19	19.0
2750	5.72	1.23	22.0
4200	3.75	1.24	24.9

Mean: $K_{mol.}$ = 0.00027; $K_{neg.ion}$ = 19.8

[1] *Vide* Dr. Schlesinger's article for a second mathematical demonstration leading to the same conclusion.

[2] The data given in Tables I. and III. were obtained with Mr. Derby, and those in Table II. with Mr. Schlesinger.

Table II.—Methyl Imidobenzoate at 25°.

N/83.3. w = 25 cc.

t.	v_t.	4343 $K_{mol.}$	$K_{neg.ion.}$
0	3.00	....	....
122	2.90	12.0	36.0
464	2.54	15.5	48.7
1489	2.00	12.0	39.3
1926	1.80	11.5	39.3
3191	1.34	10.1	40.4
4260	1.00	11.2	44.7

Mean: $K_{mol.}$ = 0.00026; $K_{neg.ion}$ = 40.7

Table III.—Ethyl Imidobenzoate at 25°.

N/40. w = 25 cc.

t.	v_t.	4343 $K_{mol.}$	$K_{neg.ion.}$
0	6.19	1.18	16.82
350	5.63	1.18	16.82
1110	4.57	1.19	17.88
1580	4.01	1.19	18.60
2480	3.04	1.24	20.86
3220	2.43	1.26	22.44
3940	1.98	1.25	....
5380	1.38	1.21	25.26
6800	0.96	1.19	....

Mean: $K_{mol.}$ = 0.00028; $K_{neg.ion}$ = 20.3.

A consideration of these tables bears out the discussion given under (1) and (2): the values for $K_{neg.ion}$ are different for different concentrations of the base, as given in Tables I. and II., and they are much larger than the real values of the constants, as determined by Schlesinger in alkaline solution; the true value of $K_{neg.ion}$ for the methyl ester is 1.97, and for the ethyl ester it is 0.69.

On the other hand, in every case good constants, $K_{mol.}$, are obtained if the reacting mass of the substance decomposing into nitrile and alcohol be referred to the nonionized imidoester present, even for a time interval of 100 hours. The reaction velocities for such a decomposition are very small, very much smaller than the constants obtained for the decomposition of the negative ion into the same products, a nitrile and an alcohol; for the methyl ester, for instance, the

decomposition constant of the molecules is only 1/7000 as large as the decomposition constant of its negative ion.

VIII. The Salt Effect.[1]

The acceleration by acids of the decomposition of imidoesters into acid esters and ammonia having been found proportionate to the salt formed by the acid with the imidoester, and the salts of imidoesters being very largely ionized in the dilute solutions used, it was thought probable that the reacting component was not all the imidoester salt but only the ionized part, *i. e.*, its positive ion.[2] In order to test this view Schlesinger has determined the velocities of decomposition for the hydrochlorides of methyl and ethyl imidobenzoate in solutions ranging from 0.05 to 0.5 molar at 25°, and has determined the degrees of ionization of these salts by conductivity methods. As was expected, the velocity constants, calculated for the total salt, showed a decided falling off with the increase of concentration and the consequent decrease of the degree of ionization; for the methyl ester, the constant fell from 0.00557 in 0.05 molar solution to 0.00477 in 0.5 molar solution, and for the ethyl ester from 0.00313 to 0.00246 for the same change in concentration. If the velocity constant referred to the total salt is called K_{salt} and α is the degree of ionization of the salt in the solution in question, then the velocity constant K_{ion}, referred to the ion concentration, as expressed in the fundamental equation of this theory of catalysis,

$$\frac{dx}{dt} = K_{ion} \times C_{pos.ion} \times C_H \times C_{OH} \qquad (22),^3$$

is

$$K_{ion} = \frac{K_{salt}}{\alpha} \qquad (23).$$

If there were no other accelerating or retarding force involved when the decomposition occurs in solutions of different

[1] This is a preliminary statement on the subject.

[2] See also the development for the catalysis of methyl acetate, Vol. *IV*, 281, Congress of Arts and Science, St. Louis (1904); THIS JOURNAL, **39**, 29 (1908); and the papers by Dr. Blunt and Dr. Hall.

[3] $C_{pos.ion}$ is a function of x.

concentrations, then K_{salt}/α should be a constant for the whole series of determinations. As a matter of fact, the values for K_{salt}/α in the determinations made with methyl and ethyl imidobenzoate formed a rapidly rising series as the solutions became more concentrated. This led to the suspicion that a second accelerating force is involved in the catalysis and it being well known that the catalysis of methyl acetate, cane sugar, etc., is subject to a decided acceleration by the presence of electrolytes,[1] a similar "salt effect" was suspected in the parallel case of the catalysis of these imidoesters. The imidoester salt itself, as an electrolyte, could have this effect in its own catalysis. The decomposition of a substance like cane sugar is accelerated from 100 to 150 per cent by a gram equivalent of ionized electrolyte, according to preliminary calculations made with Arrhenius' data, and so decidedly rising values for K_{salt}/α cease to be surprising.

One of the chief criteria of such salt effects is that, except for extremely dilute solutions, the acceleration produced is proportionate to the concentration of the electrolyte or, better, is proportionate to the concentration of the ionized portion of the electrolyte which is present. Considering the results for K_{salt}/α from this point of view, we soon found that the values showed, in fact, an acceleration of the action directly proportionate to the concentration of the electrolyte, *i. e.*, to the ionized portion of the imidoester salts themselves.

By plotting the values for K_{salt}/α and the concentrations of the ionized part of the salt, C_{ion} (the concentration of the positive or the negative ion present), on coördinates, a rectilinear curve is obtained and the velocity constant K_o for the imidoester ion alone, without any salt acceleration, can then be found by prolonging the curve to a point corresponding to a value for $C_{ion} = 0$. This value K_o having been found, the effect of the salt acceleration can be simply expressed in

$$K_{ion\ (theor.)} = K_o (1 + \beta C_{ion}) \qquad (24),$$

in which β is the acceleration produced by 1 gram equivalent ionized salt per liter, and C_{ion} is the concentration of the

[1] Arrhenius: Z. physik. Chem., **1**, 126 (1887); **4**, 235 (1889). Euler: *Ibid.*, **33**, 348 (1900), etc.

ionized part of the salt present. The equation represents an acceleration proportionate to the ion concentration and $K_{ion\ (theor.)}$ should agree with the experimental value $K_{ion\ (found)}$ or K_{salt}/α.

The acceleration β is about 100 per cent per gram equivalent ionized salt for the hydrochloride of the methyl ester, *i. e.*, about of the same order as found for the salt effect on other catalytic actions. For the ethyl ester, it was found to be smaller, but the results with the methyl ester are considered the more reliable.

For a quantitative study of this salt effect thus discovered, very exact determinations of the degrees of ionization of the imidoester salts are of particular importance; they must be more exact than the determinations originally made by the ordinary methods in vogue could be considered to be. And so a careful investigation of this part of the subject was undertaken by Dr. Barnard; the effects of various added salts—potassium, sodium, and lithium chloride—were studied in mixtures prepared on the basis of the principle of isohydric solutions and the determinations of the degrees of ionization were checked by conductivity determinations of mixtures also prepared according to the principle referred to. A more detailed discussion of the salt effect, as studied for the imidoesters, is therefore postponed to a later paper based on Miss Barnard's results; but before closing this preliminary statement on the subject, I wish to call attention to the following: Salt catalysis, according to the most critical views on the subject, is supposed to consist, either wholly or partly, in an effect on the ionization of water, which, according to equation (22), is one of the active substances in the decomposition of the imidoesters, as it is in the catalysis of esters and of cane sugar; at the same time, it is supposed to effect possibly, also, the active mass of the substance undergoing decomposition.[1] It is an important question to determine experimentally whether the water really is affected. Now, for the imidoesters the concentration of the imidoester ion in equation (22) can be determined reliably by experiment with the aid of the

[1] Arrhenius: *Loc. cit.* Euler: *Loc. cit.*

isohydric principle, which Miss Barnard has proved may be successfully applied to mixtures of imidoester salts with other salts. If, then, the salt effect is in truth wholly due to a change of the ionization of water (forming the other active masses in equation (22)), then the acceleration factor β (equation 24) for a gram equivalent ionized salt, such as potassium chloride, ought to be the same for the different imidoester salts at a given temperature, irrespective of the actual value of the velocity constant K_o, *i. e.*, for a slow or a fast reacting imidoester.

With the consideration of this object in mind, the results obtained with Derby and McCracken[1] on the velocity of decomposition of methyl and ethyl imidobenzoates and of ethyl imido-*m*-nitrobenzoate—the latter reacts about ten times as fast as the former—as determined in the presence of an added excess of hydrochloric acid (up to 0.5 moles) were analyzed; the degrees of ionization of the imidoester salt and of the acid were estimated on the basis of the isohydric principle and β was calculated from the values for K_{salt}/α obtained. In both cases a good agreement with the requirements of equation (24) was found, and β was found to have the same value for the two esters which have such different velocity constants. For methyl imidobenzoate β was found to be 109 per cent; for the ethyl ester, 107 per cent; and for the ester of nitrobenzoic acid, 110 per cent.[2]

IX. The Velocities of Decomposition of the Imidoester Ions and the Affinity Constants of the Imidoesters.

The decomposition of an imidoester according to

$$RC(:\overset{+}{N}H_2)OR' + HOH \rightarrow RCOOR + \overset{+}{N}H_4 \qquad (25)$$

represents the formation of an ion, NH_4, of a stronger base, ammonium hydroxide, from the positive ion of a weaker base, the imidoester. A general tendency of actions to take place in this direction in the presence of acids having been observed,

[1] See their papers in later numbers of THIS JOURNAL.

[2] Dr. Barnard's more exact determinations of the degrees of ionization of the imidoester salts modify the numerical values of these factors very much, but relatively in the same way. Our more rigorous experimental test of the above question answers it, more reliably, in the same sense.

and being, indeed, noticeable in all fields of chemistry, it was thought desirable to determine whether the difference between the affinity constant of the imidoester and that of ammonia affected also the speed of the above decomposition. Dr. McCracken[1] has found that the salts of the imidoesters which are the weakest bases are also decomposed most rapidly—in other words, the weaker the base from which the positive ion is derived, the greater the speed with which the latter is changed into the ion of the stronger base. For instance, for 25° we have:

Ester.	$10^5 K_{ion.}$	$10^{-9} k_{aff.}$
Ethyl imido-*m*-nitrobenzoate	3200	1.1
Methyl imidobenzoate	577	4.8
Ethyl imidobenzoate	377	11.0
Isobutyl imidobenzoate	350	12.5
Isoamyl imidobenzoate	349	16.8
Ethyl imido-β-naphtoate	251	7.9
Ethyl imido-*p*-toluylate	175	19.7

With the exception of the naphtoate, it appears, then, that the order of the affinity constants represents also the order of arrangement for the velocity constants, the latter decreasing when the former grow larger.

Euler[2] has arrived at the same conclusion for the velocity constants for the catalysis of the acid esters by making the not unreasonable assumption that the basic properties will be weakest for those esters which are derived from the strongest acids. In the case of the imidoesters such an assumption was unnecessary, as the affinity constants could be determined directly by means of the hydrolysis constants of the hydrochlorides as obtained from conductivity measurements. This similarity between imidoesters and the acid esters brings us to the last topic of our report.

X. *The Analogies between Imidoesters and Acid Esters.*

Our investigations have brought to light the following parallelism between imidoesters and acid esters:

[1] See a later paper in THIS JOURNAL, by Wm. McCracken.
[2] Z. physik. Chem., **38**, 419 (1901).

(1) The decomposition of imidoesters by water, like that of ordinary esters, is accelerated by the presence of acids, and for both cases the (catalytic) acceleration may be ascribed quantitatively to the same cause, salt, and consequent ion, formation. For both decompositions the same fundamental isothermal velocity equation holds:

$$\frac{dx}{dt} = k_v \times C_{pos.ions} \times C_H \times C_{OH} \qquad (26).$$

In the case of the imidoester, a derivative of the ammonium ion is decomposed; in the case of the acid ester, it is an oxonium ion.

(2) In both cases the decomposition results in the formation of an ion of a stronger base than the original substance was; for the imidoester (equation 20), ammonium ions are formed from imidoester ions and ammonium hydroxide is a stronger base than the imidoester. For the acid ester we have,

$$RCO.\overset{+}{O}.\underset{H}{\underset{|}{R}} + HOH \rightarrow RCOOH + H.\overset{+}{O}.\underset{H}{\underset{|}{R}} \qquad (27),$$

$$\rightarrow RCOOH + HOR + \overset{+}{H} \qquad (28),$$

the oxonium ion of alcohol resulting, and alcohols unquestionably must form stronger oxonium bases than acid esters do.

(3) In both cases the velocities of decomposition are the greatest, the weaker the original base; the weaker imidoesters are decomposed much faster than the stronger ones, and the same is true, according to Euler, for the weaker basic acid esters (see above).

(4) This decomposition of imidoester ions by water is accelerated by electrolytes (salt effect), just as is the decomposition of the acid esters. In both cases we probably have to do with an increase in the ionization of water.

(5) Imidoesters, like acid esters, are decomposed (catalytically) by alkalis, and for both reactions the same fundamental equation,

$$\frac{dx}{dt} = K_v \times C_{neg.ions} = K'_v \times C_{ester} \times C_{OH} \qquad (29),$$

again holds, *i. e.*, the velocity of decomposition is proportionate to the concentrations of the ester and the hydroxyl ion. In both cases the velocity constants for decomposition in alkaline solution are greater than for acid solutions.

(6) Neighboring (ortho) alkyl groups interfere both with the esterification of the aromatic acids and with the saponification of their esters. Pinner found, likewise, that neighboring alkyl groups interfere with the formation of imidoesters from nitriles, and we have confirmed his results for *o*-tolunitrile and for *β*-naphtonitrile,[1] and have found, besides, that the decomposition by water of such an imidoester, once prepared from the silver salt of an acid amide, is also very perceptibly retarded by the neighboring group. For ethyl imido-*o*-toluylate the velocity constant is 0.00128, as compared with 0.00175 for the *p*-toluylate, whereas the *o*-toluylate, as the weaker base (the constants are 2×10^{-9} for the ortho and 2×10^{-8} for the para ester) ought to decompose the faster.

(7) Dry imidoester hydrochlorides are decomposed at ordinary temperature or by moderate heat, say at 120°–130°, into alkyl chlorides and acid amides, according to

$$RC(:NH_2Cl)OH_3 \rightarrow RCONH_2 + CH_3Cl \qquad (30).$$

Dry acid esters, treated with hydrogen chloride, also give alkyl chlorides, according to

$$RCO.O.CH_3 \underset{HCl}{\rightarrow} RCOOH + CH_3Cl \qquad (31).$$

The chief point of difference between imidoesters and acid esters lies in the more pronounced basic properties of the former and the formation of salts which are comparatively little hydrolyzed—a difference which is invaluable for the experimental study of catalytic action, but still is only a difference of degree and not of nature.

A reply to Mr. Acree's remarkable article in the January number of THIS JOURNAL will appear in the March number.

CHICAGO, September, 1907.

[1] McCracken: *Loc. cit.*

ON SOME CUPRAMMONIUM SALTS. V.[1]

By David Wilbur Horn.

The object of the experiments described in this paper was to obtain definite information concerning the influence of the acid residues upon the complexity and stability of cuprammonium salts. The result of most general interest is the arrangement af 9 well-known acids in the order in which they favor the formation of copper-ammonia complexes.

Cuprammonium salts of the same degree of complexity containing different acid residues are not equally stable. This fact was pointed out in the second paper of this series.[2] The difference was illustrated by these salts:

$$CuSO_4 + 4NH_3 + H_2O,$$
$$Cu(NO_3)_2 + 4NH_3.$$

Reychler's values[3] for the molecular lowering of the freezing point and for the equivalent conductivity of these two salts in aqueous solution are quite different. There is a marked difference also in Blanchard's values[4] for the viscosity of their aqueous solutions and for the effect of ammonia upon it.

The cause of the differences might lie in the acid residue or in the "water of crystallization." The importance of this last factor could not be estimated. Experiment has shown that the union with the water is a most intimate one. The sulphate has been kept unchanged over lime for one year[5] and even in a vacuum over phosphorus pentoxide for a week at a time.[6] If it is heated to drive off the water, two ammonia groups leave the molecule at the same time.[7] To eliminate this uncertain factor, "water of crystallization," in my experiments, water was excluded.

[1] Read in abstract at the meeting of the American Chemical Society at Toronto, June 28, 1907.

[2] This Journal, **35**, 272 (1906).

[3] Ber. d. chem. Ges., **28**, 555 (1895).

[4] J. Am. Chem. Soc., **26**, 1315 (1904).

[5] Horn and Taylor: This Journal, **32**, 267 (1904).

[6] Horn: *Ibid.*, **38**, 477 (1907).

[7] Sabbatani: Jahres. d. Chem., **1**, 960 (1897). Horn and Taylor: *Loc. cit.*, p. 272.

The guide in this work has been the Phase Rule. Definite and comparable results may be obtained, as has been shown,[1] by selecting one temperature for all of the experiments and preparing the salts, to be studied later, in systems where copper salt, ammonia, and water are always present in the same molecular ratio.

Any molecular ratio of the 3 components,

$$x \text{ mol } Cu(Ac)_n : y \text{ mol } NH_3 : z \text{ mol } H_2O,$$

may be selected, just as any temperature will do, provided it be maintained invariable throughout. I adopted a ratio in which $z = 0$ for the reason already given, *i. e.*, to exclude possible effects due to "water of crystallization." Any such ratio has the further advantage of experimental simplicity, for at all temperatures above the boiling points of the saturated solutions of the several cuprammonium salts in liquid ammonia the systems will consist only of a solid phase and a gas phase. In the solids, the ratio of the components will adjust itself automatically in accordance with the Law of Definite Proportions; and when this has occurred y may be maintained at a constant value very simply by working at any constant pressure.

Such a system, in which $z = 0$, is one of the limiting cases of a system originally ternary and divariant, containing one solid, one liquid, and one vapor phase, like those in which cuprammonium salts are usually prepared from aqueous solutions, and like the one worked out experimentally in considerable detail and described in the third paper in this series.[2] Since it is very doubtful if the last traces of water are ever excluded by observing any of the usual precautions, z probably never equals zero in my experiments but only approaches to it in value. The equality sign has been used in this sense. Although virtually the systems are binary when z becomes vanishingly small, there is no real gain in simplicity in so regarding them; for as the liquid phase disappears when the component water vanishes, they remain divariant at all temperatures above the boiling points of the saturated

[1] Horn: THIS JOURNAL, **37**, 475ff. (1907).
[2] *Ibid.*, **37**, *loc. cit.*

solutions of the several cuprammonium salts in liquid ammonia. On the other hand, there is a real loss in considering such systems as binary, for the ultimate relation to the more usual ternary systems which have yielded most of the cuprammonium salts is in this way obscured.

From both points of view, the method of study is the same. One must obtain different solid cuprammonium salts that exist *in stable equilibrium* with gaseous ammonia at some one temperature and pressure and then compare them as to complexity and stability. Since the systems all contain the same metallic element, copper, and the same gaseous substance, ammonia, under the same conditions of temperature and pressure, they are identical except as to the nature of the acid residue. The difference in properties, therefore, that the systems may exhibit can only be referred to the difference in the acid residues. The most striking differences actually exhibited by the systems are in the complexity and stability of the cuprammonium salts that appear as the solid phases when equilibrium exists in each of the systems. Consequently the complexity and stability must be functions of the nature of the acid residue. The word function is used in the same sense as in the statement that "the properties of an element are functions of its atomic weight."

The salt which, in equilibrium at the given temperature and pressure, has the largest number of ammonia groups in it, certainly contains that acid residue which is most favorable to the formation of complexes, while the salt that, under the same conditions, has the smallest number of ammonia groups in it, contains an acid residue least favorable to the formation of complexes. Between these limits must be placed the acid residues occurring in salts that, under the same conditions, contain an intermediate number of ammonia groups. Of all the acid residues occurring in several salts that, under the same conditions, are found to contain the *same* number of ammonia groups, the one most favorable to the formation of complexes occurs in the salt that is most stable, and the one least favorable to the formation of complexes in the salt that is most unstable.

The relations between complexity and stability and the nature of the salt, and the dependence of the final results on the choice of temperature and pressure are brought out clearly by the aid of a graph. For the ammonia compounds of each copper salt, the solid-solid-vapor lines, *i. e.*, those of the space model representing the entire system as binary, when projected on the temperature-pressure plane, will give curves resembling those in the figure. The graph is a diagrammatic

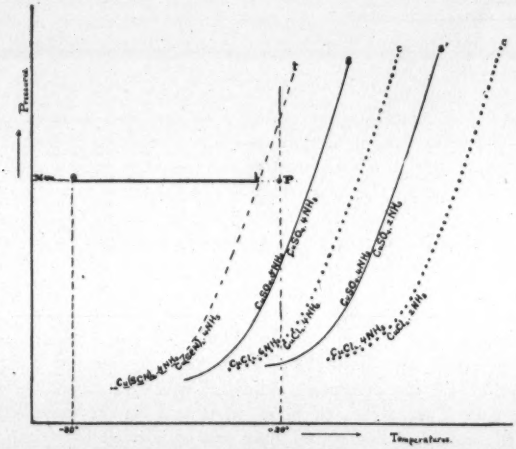


Fig. 1.

representation of the "vapor pressure curves" or "curves of dissociation tensions" of the compounds of three different salts, the sulphate, sulphocyanate, and chloride. The general form of the curves is represented as the same in all cases and is identical with that of the ordinary vapor pressure curves of pure liquids, like water. This is a direct inference from Isambert's measurements[1] of the dissociation tensions of the ammonia compounds of a number of salts.

[1] Compt. rend., **66**, 1259 (1868); **70**, 456 (1870). Ladenburg: Handwörterbuch d. Chem., **3**, 400.

Each curve in the diagram represents the pressures and temperatures of equilibrium between two solid cuprammonium salts and ammonia gas. The formulae of the two solids are written in each case along the curve. The areas between the curves represent the pressures and temperatures of equilibrium between one solid cuprammonium salt and ammonia gas. When the relative position of these curves with respect to each other and to the axes is known, all data concerning the preparation and relative stabilities of the anhydrous cuprammonium salts is at once available.

An area to the left of a curve represents the conditions for the stable existence of the more complex of the two salts written along the curve, and the area to the right of the same curve, the conditions of stability of the less complex one. To illustrate this, if anhydrous copper sulphate is placed in ammonia gas at a temperature and pressure represented by any point within the area to the left of the curve S, and to the right of the vertical axis erected at the boiling temperature of liquid ammonia, the pentammine sulphate must be formed. If the pentammine sulphate, still in contact with ammonia gas, is brought to a temperature and pressure represented by any point to the right of S or to the left of S′, it will decompose into the tetrammine sulphate.[1] If the pressure and temperature are maintained at values represented at the right of S′, the diammine sulphate[2] will be formed. When the curves are given, to know what will be the complexity of the ammonia compound that will be formed by a copper salt when placed in ammonia gas at some one temperature and pressure, it is only necessary to locate the point in the diagram that corresponds to the selected temperature and pressure and then to see within what area it lies. For example, when the temperature and pressure are such as to be correctly represented by a point located at P, it is evident at a glance that, under these conditions, a hexammine chloride, a pentammine sulphate, and a tetrammine thiocyanate would be formed, and that compounds of other than these

[1] Bouzat: Ann. Chim. Phys. [7], **29**, 330 (1903).
[2] *Ibid.*

degrees of complexity could have no stable existence until the conditions were changed from those represented by P to those represented by some other point in the diagram.

The point P clearly represents an *arbitrary* selection of conditions, but if it is placed, as it has been, at the average laboratory temperature, +20° C., and the average atmospheric pressure, 76 cm., the selection need not be considered arbitrary because the point P then represents the conditions under which the larger number of chemical facts have been established and studied.

It is evident from the diagram that, if too high a temperature is selected for the experiments, in some cases P might fall on, or to the right of, the curve of the most complex ammonia compounds of one or more copper salts. In such cases compounds capable of existence would never enter into consideration, for they would remain undiscovered. It is a familiar fact that the highest ammonia compound of silver chloride remained unknown until Isambert happened to treat silver chloride with ammonia at temperatures *below* +20° C.; in this case, P, when representing atmospheric pressure and the average laboratory temperature, falls almost exactly upon the curve for the compounds $AgCl.2NH_3$ and $2AgCl.3NH_3$.[1] The diagram shows that the pentammine sulphocyanate would never have been discovered in the course of my experiments if they had all been made at the temperature of the room. The same is true of other compounds mentioned later.

To avoid being misled in such cases, and to make the basis of the work less arbitrary, I selected for my experiments atmospheric pressure and temperatures above the boiling points of the saturated solutions of the copper salts in liquid ammonia, about −30° C., and below the transition point at 76 cm. of the most unstable salt that could be dealt with conveniently with the facilities in this laboratory. These conditions are represented in the diagram by the heavy line, *ab*.

To illustrate the reasoning followed in arranging the acids in the order in which they favor the formation of copper-

[1] Isambert: *Loc. cit.* Cf. Horstmann: Ber. d. chem. Ges., **9**, 756 (1876), and Horn: THIS JOURNAL, **37**, 626 (1907).

ammonia complexes, the data in the diagram may be used as follows: Hydrochloric acid, which appears in a hexammine salt, must be placed first, because no dissociation curve corresponding to a hexammine sulphate or thiocyanate exists at temperatures above −30° C. and pressures below 76 cm. Sulphuric acid must be placed before sulphocyanic acid, although both appear in pentammine salts, because the curves show that at any temperature the pentammine sulphocyanate, when dissociating, has a higher tension of ammonia over it than the pentammine sulphate, or, conversely, that at any pressure the pentammine sulphocyanate dissociates at a lower temperature than the pentammine sulphate. This method of reasoning is followed later.

The experiments described in this paper are not the first in which the action of ammonia on copper compounds has been investigated. Several isolated experiments of this kind had been carried out by others. The compounds that had already been made by the action of ammonia gas on anhydrous copper salts have the formulae:

$CuCl_2.6NH_3$,[1] $CuSO_4.5NH_3$,[2]
$CuBr_2.6NH_3$.[3]

A short time ago I described several new cuprammonium oxalates, obtained from solution, and the one of these with the largest number of ammonia groups has the formula $Cu(OOC)_2.5NH_3$.[4] In considering this along with the three other formulae just given, it was noticed that there are but 5 ammonia groups per molecule where the acid residue is dibasic, and 6 where the acid residue is monobasic. A similar relation was noticed in a comparison of the compounds of the same 4 salts with the smallest possible number of ammonia groups.

The formulae of these compounds are:

$CuCl_2.2NH_3$,[5] $CuSO_4.NH_3$,[6]
$CuBr_2.2NH_3$,[7] $Cu(OOC)_2.NH_3$.[8]

[1] H. Rose: Pogg. Ann., **20**, 155 (1830).
[2] T. W. Richards: Ber. d. chem. Ges., **23**, 3790 (1890).
[3] H. Rose: *Loc. cit.*, p. 150.
[4] This Journal, **35**, 279 (1906).
[5] Bouzat: *Loc. cit.*, p. 332.
[6] T. W. Richards: *Loc. cit.*
[7] Bouzat: *Loc. cit.*, p. 331.
[8] Horn: *Loc. cit.*, p. 276.

A *monammine* chloride or bromide can not be made from the corresponding *diammine* salt, although the monammine sulphate is made in that way.[1] When the diammine salts of either of the monobasic acids is heated in an endeavor to dissociate it into a monammine salt, the whole molecule is destroyed.[2]

Another example of the different influence of monobasic and dibasic acid residues was found in the ammonia compounds of cobalt and chromium. A dibasic acid residue appears not only in tetrammine salts analogous to the tetrammine salts containing two monobasic acid residues per molecule, as might be expected according to the ideas of Werner, but it also appears in *pentammine* salts.[3] These pentammine salts are *not* analogous to the pentammine salts containing one monobasic acid residue, *i. e.*, the purpureo salts. Werner and Gosling's statement[4] that *a dibasic acid residue may occupy two or one coördination places* does not explain this unexpected fact. It is *apropos* to remark that cases in which two monobasic acid residues together occupy one coördination place are not met with in the 110 groups of hexammine, pentammine, and tetrammine cobalt and chromium compounds that are now known.

It seemed most important, then, at the outset, to determine experimentally whether or not the largest number of ammonia groups that can combine with copper salts is a function of the *basicity* of the acid residue. The data for each copper salt are taken up under a separate heading. As my work has been interrupted for a time, many new facts besides those germane to the principal result of the investigation have been included under some of the headings.

I. Copper Sulphate.

Perhaps the most curious among the accumulated facts regarding cuprammonium salts is that copper sulphate has

[1] Bouzat: *Loc. cit.*

[2] Bouzat: *Loc. cit.*, p. 332. T. W. Richards: *Loc. cit.*, p. 3790.

[3] $[Co(NH_3)_5.SO_4]X$. Jörgensen: J. prakt. Chem. [2], **34**, 262 (1885).
$[Co(NH_3)_5C_2O_4]X$. Jörgensen: Z. anorg. Chem., **11**, 418 (1896).
$[Co(NH_3)_5.SO_3]X$. Werner and Grüger: Z. anorg. Chem., **16**, 403 (1898).
$[Co(NH_3)_5.CO_3]X$. Werner and Goslings: Ber. d. chem. Ges., **36**, 2378 (1903).

[4] Werner and Goslings: *Loc. cit.*

never been known to combine with more than *five* ammonia groups. The ideas of Werner cannot account for this fact[1] which is irreconcilable with all views based upon analogy. The pentahydrate Werner represented as $[Cu(H_2O)_4]SO_4.H_2O$, ascribing the presence of the fifth molecule to the affinity of sulphuric acid for water.[2] It is difficult to conceive of the existence of the anion which we must assume if the pentammine salt is represented by an analogous formula and is ionized:

$$[Cu(NH_3)_4]\,SO_4.NH_3 \rightleftharpoons Cu(\overset{+}{N}H_3)_4 + SO_4.\overset{=}{N}H_3.$$

Mendelejeff evidently doubted the inability of copper sulphate to combine with more than 5 ammonia groups, for he states he convinced himself that no more than 5 groups can be added.[3] Bouzat found that the pentammine salt remained after anhydrous copper sulphate had been treated with an excess of liquid ammonia and the liquid allowed to boil off at atmospheric pressure.[4] But Mendelejeff does not state throughout what range of conditions he made the test, and the data for his experiments are not available. Bouzat's experiments do not prove that at temperatures *below* that of his laboratory more than 5 groups may not have been combined with the copper sulphate. Although the only other substance described, up to the time this work was begun, as a *pentammine* cuprammonium salt, *i. e.*, $CuBr_2.5NH_3$,[5] had been shown by T. W. Richards[6] to be a hexammine salt, yet a sulphate analogous to the hypothetical hexa-ammonia sulphate, namely, $CuSO_4.3[C_2H_4(NH_2)_2]$,[7] had been described by Werner.

A final answer can be given in all such cases by means of the method for determining transition points recently described.[8] When a thermometer is immersed in the mixture obtained by drawing anhydrous liquid ammonia upon an

[1] Horn: THIS JOURNAL, **35**, 280 (1906).
[2] Z. anorg. Chem., **3**, 309 (1893).
[3] "Principles of Chemistry," Trans. 6 Russ. Ed., II., 363, footnote 35.
[4] *Loc. cit.*
[5] Rammelsberg: Pogg. Ann., **55**, 246 (1842).
[6] Ber. d. chem. Ges., *loc. cit.*
[7] Z. anorg. Chem., **21**, 219 (1899).
[8] Horn: THIS JOURNAL, **37**, 619 (1907).

anhydrous copper salt, the system being so arranged that it communicates with the air only through a delivery tube dipping just beneath the surface of mercury, *i. e.*, so that a constant pressure of about 1 atmosphere is maintained, it is possible, by observing the thermometer, to tell whether the same solid compound existing at the temperature at which the saturated solution boils persists until the whole system has acquired the temperature of the room, or whether it decomposes to form a simpler one at intermediate temperatures. With constant pressure, as long as liquid ammonia is present the reading of the thermometer is constant, for the system is monovariant.[1] The instant the liquid disappears the system becomes divariant and the temperature begins to rise and continues to do so until the system acquires the same temperature as its environment, or until the system again becomes monovariant by the formation of another phase, *i. e.*, a new solid compound formed by the decomposition of the first compound. It is impossible for a new compound to be formed in such a divariant system without changing it to a monovariant one, thus causing a halt in the rise of temperature. Conversely, each halt in the rise of temperature after the liquid ammonia is entirely gone indicates a decomposition of a more complex into a less complex compound, and the absence of any such halt is *prima facie* evidence that the same compound that is stable at the temperature of the room is stable at the boiling point of the saturated solution in liquid ammonia.

The method followed in getting the data and interpreting them is very simple and is the same in all cases. It has already been sufficiently discussed.[2] Since the form of the curves is identical in all cases it is unnecessary to give the graph for every one. It is sufficient to state whether or not each case has been tested by this method, and if so, whether or not the curve indicated the persistence of a divariant system throughout the whole range included between the average temperatures of $-30°$ C. and $+20°$ C.

[1] Two components: copper salt and ammonia; three phases: *solid* cuprammonium salt, saturated solution of cuprammonium salt in *liquid* ammonia, ammonia *vapor*.

[2] Horn: *Loc. cit.*

When the method was applied to copper sulphate and ammonia, the form of the curve was found to be that of a divariant system throughout. Therefore, *at all pressures not greater than one atmosphere and all temperatures between approximately* $-30°$ *C. and* $+20°$ *C.* the hypothetical hexammine sulphate is incapable of existence, and *copper sulphate cannot combine with more than 5 ammonia groups.*

When anhydrous copper sulphate is placed in dry ammonia gas there is often considerable difficulty in obtaining complete addition. Bouzat found that after six hours only 4.8 mol. of ammonia had been taken up, and we have found cases of incomplete addition after 16 hours. Upon the basis of a wide experience, which cannot be described here in detail, I attribute this to some impurity in the copper sulphate. I have found repeatedly that unless extraordinary precautions are taken to reduce the amount of iron present in the pentahydrate to a minimum, the anhydrous salt prepared from it is mixed with basic salts or other products of hydrolysis. I have tried removing four-fifths of the water at the boiling point of water, and also at the boiling point of alcohol, both at atmospheric pressure and at full vacuum of a good filter pump—about 2 cm.—and raising the temperature very gradually in some cases and very quickly in others. With the same range of conditions, I have tried removing the last molecule of water in an atmosphere of air previously passed through fuming sulphuric acid. In some cases a brownish product was obtained even when the salt, after repeated recrystallizations, was dehydrated by heating in contact with sulphuric acid of sp. gr. 1.84. Fusing with ammonium sulphate and volatilizing the excess of it[1] yielded a brownish product also. On the other hand, a copper sulphate containing but a few thousandths of a per cent of iron, such as "Kahlbaum's C. P.," yields a white anhydrous product when heated at atmospheric pressure in a current of dry air. When this is placed in dry ammonia gas at one atmosphere, it adds 5

[1] Klobb: Cmpt. rend., **114**, 836 (1892).

molecules of ammonia in somewhat less than 5 hours. The following are the analyses made in such an experiment:

Table I.—Analysis of the Anhydrous Copper Sulphate.

Weight taken for analysis. Gram.	Weight of cuprous sulphide found. Gram.	Percentage of copper found.	Percentage calculated for $CuSO_4$.
0.7896	0.3928	39.73	39.82
0.4395	0.2187	39.73	....

Table II.—Analysis of the Addition Product.

Weight taken for analysis. Gram.	Volume of acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $CuSO_4.5NH_3$.
0.2992	28.65	34.84	34.81
0.3612	34.50	34.75	....
	Weight of cuprous sulphide found.	Percentage of copper found.	
0.3472	0.1127	25.94	25.96
0.2722	0.0884	25.93	....

Mendelejeff is reported[1] to have stated that the pentammine sulphate does not lose any ammonia when placed over concentrated sulphuric acid. This is an error. Under such conditions this sulphate loses weight continuously for at least 3 months. Specimen data showing this are given below, in this paper.[2]

II. Copper Oxalate.

The principal question to be answered here is whether or not copper oxalate can combine with more than 5 ammonia groups.

Anhydrous copper oxalate has not yet been described. Hydrated copper oxalate cannot be completely dehydrated without further decomposition.[3] The crystallized pentammine oxalate,[4] although anhydrous when prepared from aqueous solutions, is extremely unstable and it is difficult, by this method, to obtain it pure, dry, and in a finely divided condition. Accordingly the anhydrous monammine oxalate[5]

[1] Ber. d. chem. Ges., **3**, 422 (1870).
[2] Page 200.
[3] Seubert and Rauter: Ber. d. chem. Ges., **25**, 2825 (1892).
[4] Horn: *Loc. cit.*
[5] *Ibid.*

was used in these experiments. The best conditions for its preparation will be given in the next paper in this series.[1]

When the monammine salt, $Cu(OOC)_2.NH_3$, is placed in dry ammonia gas, the color at once begins to change and the weight increases somewhat over 39 per cent during the course of 24 hours or more, after which it remains practically constant. The formation of the pentammine salt requires a gain in weight of 40.46 per cent. While the monammine salt is green, the addition product is purple-blue. It was analyzed, with the following results:

Weight taken for analysis. Gram	Volume of acid neutralized cc.	Percentage of ammonia found.	Percentage calculated for $Cu(OOC)_2.5NH_3$.[2]
0.2986	28.72	35.88	36.01
0.2106	20.69	35.66	....

When the transition point method was applied to mixtures of the pentammine oxalate obtained in this way and liquid ammonia, or to mixtures made by drawing liquid ammonia upon the monammine oxalate, the form of the curves, from about $-30°$ C. up, was found to be that of a divariant system throughout. Therefore, *at all pressures not greater than one atmosphere and all temperatures between approximately $-30°$ C. and $+20°$ C., no more than 5 ammonia groups can be added to each molecule of copper oxalate.*

The source of dry ammonia gas that we used in the work with the oxalate is so generally useful for experiments when liquid ammonia is not available that it seems desirable to describe it briefly. Ammonia gas, obtained by warming ammonia water in a flask with a return condenser, was passed over some two meters of freshly broken potassium hydroxide and then through solid dry ammonium nitrate in a Drechsel bottle. The bottle was immersed in a mixture of ice and salt and water, and the outlet tube protected from moisture by a tube of freshly broken potassium hydroxide. Under these conditions the ammonia is absorbed to a large extent

[1] VI. On Isomeric Oxalates.

[2] I am indebted to Miss E. Helen Lundie for making these experiments and the analysis.

and the ammonium nitrate fuses. The resulting *solution*[1] can be made of any desired concentration, within certain limits, and can be so prepared as to furnish dry ammonia at any desired temperature, at a pressure proportional to the concentration. This holds true so long as the concentration of ammonia is so high that the solution is not saturated with ammonium nitrate. If the concentration is such that solid ammonium nitrate separates, or does not completely dissolve, the system is then monovariant and at each temperature can furnish the gas at but one pressure. This liquid, first described by Divers,[2] is most useful in studies of the addition of ammonia to solid salts as well as in many other experiments involving the use of dry ammonia gas. A good many measurements of the concentrations, temperatures, and pressures of this system are already available in the literature.[3]

We preserved this liquid by sealing it up in test tubes, which could be readily broken in suitable apparatus when desired. With sufficient care and attention to thermal insulation, it is possible to seal up solutions containing from 45 to 75 grams of ammonia to each 100 grams of ammonium nitrate. Of course, it is more convenient, where possible, to prepare the solution by adding anhydrous liquid ammonia to dry ammonium nitrate in a freezing mixture.

The form of apparatus represented in Figure II. proved very convenient. The vacuum desiccator contains the copper compound that is to be studied, in a weighing tube having a base of large area. The lid of the desiccator is held in position by bolts passing through two pieces of wood, as shown. The tube A contains the solution of ammonium nitrate in ammonia, sealed up in a test tube. The outlet 3 is connected to a good filter pump through a Drechsel bottle containing enough mercury to prevent the backward diffusion of water vapor. The whole apparatus is evacuated to the limit attain-

[1] Kuriloff: J. russ. chem phys. Ges. [1], **25**, 170 (1893). Z. physik. Chem., **25**, 107 (1898).

[2] Phil. Trans., **163**, 359 (1873). Cf. Raoult: Compt. rend., **76**, 1261 (1873).

[3] Divers: *Loc. cit.* and Z. physik. Chem., **26**, 430 (1898). Raoult: *Loc. cit.* and Compt. rend., **94**, 1117 (1882). Troost: Compt. rend., **94**, 789 (1882). Kuriloff: *Loc. cit.*

able by the pump, about 2 cm.; cocks 3 and 2 are then closed, and the tube A suddenly brought into a vertical position. The test tube breaks when it strikes the lower end of A, and A immediately fills with dry ammonia. Cock 2 is now opened cautiously and the whole apparatus allowed to fill with ammonia. Cock 2 is again closed, and the apparatus once more evacuated; then 2 is opened and the apparatus again filled with ammonia. When the ammonium nitrate solution no

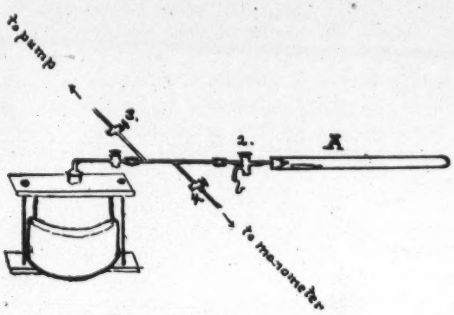


Fig. 2.

longer supplies ammonia at a sufficient pressure, as indicated by the manometer, cock 2 is closed, another tube, A′, containing a fresh test tube of solution is substituted for A, the pump is connected at *b* until A′ is evacuated, the test tube is broken as before, and the pressure in the whole apparatus brought to the desired point by proper manipulation of the cock 2. Cock 4 is kept closed except when making measurements of the pressure.

III. Copper Succinate.[1]

Anhydrous copper succinate was obtained by heating to constant weight at +150° C. the product obtained when hot dilute solutions of copper sulphate are added to hot dilute

[1] I am indebted to Misses E. E. Van Wagner and E. H. Lundie for the experiments on the succinates.

solutions of ammonium succinate. When placed in dry ammonia gas the color of the anhydrous salt at once begins to change and its weight increases somewhat over 46 per cent during the course of 18 hours or more, after which it remains practically constant. It is *essential* that the dehydration should be complete, and special attention must be given to this because it is difficult to dry the salt completely. Prolonged heating at +150° C. does not injure the succinate and does accomplish a complete dehydration. A specimen that had been exposed to the air several months increased only about 23 per cent in weight in dry ammonia gas, whereas 1.1763 grams of a dry specimen gained 0.5426 gram, or 46.13 per cent. The formation of the compound $Cu(OOC)_2C_2H_4.5NH_3$ from the anhydrous salt requires a gain of 46.46 per cent. The anhydrous salt is green; the addition product, purplish-blue.

When the transition point method was applied to mixtures obtained by treating *this pentammine succinate* with liquid ammonia, this same salt *was found to be the only one that exists between approximately −30° C. and +20° C.*

The pentammine succinate, like the sulphate, loses ammonia in a desiccator over sulphuric acid, sp. gr. 1.84. The losses in weight exhibited by the pentammine sulphate, succinate, and oxalate after different lengths of time are given in the following table. The losses have been calculated in molecules of ammonia lost per molecule of salt. The specimens were in a finely divided state and were stirred at intervals with glass rods that were not removed from the weighing tubes throughout the whole time. The tubes were closed with ground glass stoppers during weighings. The original weight of sulphate was 1.207 grams; of succinate, 1.255 grams. In the case of the oxalate, after 0.2863 gram monammine oxalate had been exposed to the action of dry ammonia gas 14 hours, it weighed 0.3876 gram. If the exposure had been continued to constant weight the weight would have been 0.0154 gram more. As the subsequent treatment was to remove ammonia, it was not considered necessary to complete the addition before beginning the decomposition. Conse-

quently 0.0154 gram was added to each loss in weight before the final calculations.

Sulphate.		Succinate.		Oxalate.	
Time in hrs.	Mols. lost.	Time in hrs.	Mols. lost.	Time in hrs.	Mols. lost.
6.5	0.12	1.0	0.32	0.0	0.53
34.0	0.36	19.0	0.87	1.5	1.67
192.0	1.11	22.0	0.97	2.0	2.09
216.0	1.13	40.5	1.18	3.75	2.64
240.0	1.16	52.5	1.25	4.5	2.82
264.0	1.18	87.0	1.30	5.5	2.91
288.0	1.20	99.0	1.32	7.0	2.96
350.0	1.21	109.0	1.34	24.5	3.08
438.0	1.28	205.0	1.42	...	....
486.0	1.29	....	....	...	....
2064.0	1.42	....	....	...	....

These data are represented graphically in Figure III.

The advantages of this graph are that the relative stabilities of the pentammine salts are apparent at a glance and

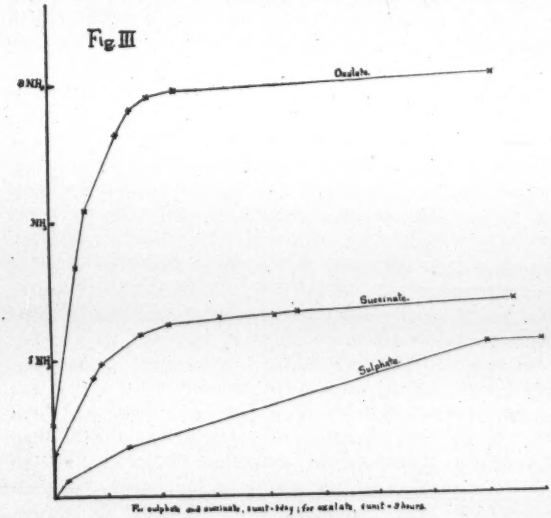


Fig. III.

that the existence of a sulphate, $CuSO_4.4NH_3$, a succinate, $Cu(OOC)_2C_2H_4.4NH_3$, and an oxalate, $Cu(OOC)_2.2NH_3$, is also indicated. The tetrammine succinate and the diammine oxalate[1] are new compounds. The tetrammine sulphate has been described by Bouzat[2] since the above data were obtained. The tetrammine succinate is of a pure, deep-blue color, lacking the purple shades of the pentammine salt.

A diammine succinate, $Cu(OOC)_2C_2H_4.2NH_3$, is formed when the pentammine salt is heated to constant weight in a current of dry air at about $+90°$ C. The following results were obtained when the residue that had reached constant weight at $+90°$ C. was analyzed:

Weight taken for analysis. Gram.	Weight of acid neutralized by the ammonia. Gram.	Percentage of ammonia found.	Percentage calculated for $Cu(OOC)_2C_2H_4.2NH_3$.
0.2036	0.09331	15.90	15.97
0.2009	0.09197	15.93	.....

An anhydrous diammine succinate was described by Schiff[3] in 1862 as the substance obtained in pseudomorphic crystals when a "dark-violet" succinate, "$Cu(OOC)_2C_2H_4.4NH_3$," gotten from solution, is heated on a water bath. Schiff's data consist in one analysis of the dark-violet crystals for copper oxide and in the percentage loss in weight shown by these crystals when heated on the water bath. Schiff's statement is erroneous.

The dark-violet succinate referred to forms so readily when copper succinate is dissolved in ammonia water that it is difficult to prevent its formation. Its color is distinctive, resembling that of potassium permanganate or violet chrome-alum, and is entirely unlike that of any other cuprammonium salt I have seen. When analyzed for ammonia the following results were obtained:

Weight taken for analysis. Gram.	Volume of acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $Cu(OOC)_2C_2H_4.4NH_3$.
0.1862	6.79	13.23	27.32
0.1228	4.61	13.61	.....
0.2251	8.47	13.66	.....
0.2019	7.66	13.77	.....

[1] See next paper in this series: On Isomeric Oxalates.

[2] *Loc. cit.*

[3] Ann. Chem. (Liebig), **123**, 45 (1862).

The percentage of ammonia found was only half of that required by Schiff's formula. To make sure that *all* of the ammonia in the compound had been determined, the substance was digested with concentrated sulphuric acid, to which phosphoric anhydride had been added, until the carbon was completely oxidized, and the residue then distilled as usual in our ammonia analyses. No blank was made for the nitrogen in the reagents. The following were the results:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia cc.	Percentage of ammonia found.	Percentage calculated for $Cu(OOC)_2C_2H_4.4NH_3$.
0.2210	8.43	13.85	27.32
0.2311	8.86	13.91	.....

The percentage of ammonia required by the formula $Cu(OOC)_2C_2H_4.2NH_3.2H_2O$ is 13.67 per cent, and the analyses leave no doubt that this is the correct formula for Schiff's dark-violet "*tetrammine*" salt. The percentages of copper oxide calculated from the two formulae are 31.87 per cent and 32.11 per cent, so that Schiff's analysis agrees with either formula.

This dark-violet succinate yields, according to Schiff, the anhydrous diammine salt at 100° C. In several experiments at +100° C. a loss of about 15.3 per cent in weight was observed, whereas the loss of the 2 water groups should amount to only 14.42 per cent, and that of 2 ammonia groups to 13.67 per cent. The residue was a blue substance in pseudomorphic crystals, as described by Schiff. Even at the temperature of boiling alcohol, the loss was about 15.3 per cent, as is shown by the first of the three following analyses. In the last two, the method[1] of determining ammonia and water previously described was used at 100° C.

Weight taken for analysis. Gram.	Loss in weight on heating. Gram.	Total percentage loss on heating.	Weight of water collected. Gram.	Weight of ammonia collected. Gram.	Percentage of water lost on heating.	Percentage calculated for $Cu(OOC)_2C_2H_4.2NH_3.2H_2O$.
0.1567	0.0240	15.30	.....	.....	.....	.....
0.9682	0.1482	15.31	0.1424	0.0070	14.70	14.42
1.0014	0.1529	15.27	0.1446	.....	14.44	....

[1] Horn and Taylor: THIS JOURNAL, *Loc, cit.*

These experiments show that when the compound $Cu(OOC)_2C_2H_4.2NH_3.2H_2O$ is heated to dehydrate it, some of the ammonia is expelled along with the water, and that Schiff's diammine salt, like the sulphates described by Kane, is a mixture.[1]

The dark-violet succinate can be obtained readily either by the spontaneous evaporation of an ammoniacal solution of copper succinate, or by the gradual addition of alcohol to this solution.

When the concentration of ammonia in the ammoniacal solution is sufficiently great, another succinate separates. This is a very soluble and unstable substance and, up to the present, I have not analyzed it.

When it had been found that the sulphate, succinate, and oxalate, all of which are salts of dibasic acids, are incapable of combining with more than 5 ammonia groups, attention was directed to salts of monobasic acids.

IV. Copper Chloride.

The well known hexammine chloride[2] was prepared from anhydrous copper chloride and dry ammonia gas. The anhydrous copper chloride was made from the crystallized dihydrate by heating to constant weight at +100° C. The dehydration is very readily accomplished within a couple of hours, although it has been denied[3] that this can be done at 100° C.

0.42016 gram of dihydrate attained a constant weight, 0.33174 gram, in 1.5 hours, the loss being 21.05 per cent, while that calculated from the formula is 21.13 per cent.

Bouzat has shown that the hexammine salt does not dissociate at atmospheric pressure until a temperature near +90° C. is reached. The transition point method, applied to the hexammine salt and liquid ammonia, showed that *the hexammine chloride is the stable form at all temperatures between the boiling point of its saturated solution in liquid ammonia*

[1] *Ibid.*
[2] Rose: *Loc. cit.*
[3] Graham: Ann. Chem. (Liebig), **29**, 21 (1841).

and +20° C. In the same way the hexammine chloride was found to dissociate under about 2 cm. pressure at +46°.7 C.[1]

V. Copper Bromide.

The hexammine bromide[2] was prepared from anhydrous copper bromide and ammonia gas. In order that the addition may be complete it is essential that the bromide should be strictly anhydrous. Before use in our experiments, the bromide was finely ground in an agate mortar and kept over phosphorus pentoxide until it no longer lost weight. The neglect of some such precaution is probably the explanation of Rammelsberg's view that only 5 ammonia groups can be added to copper bromide.

The hexammine bromide, treated with an excess of liquid ammonia, was examined by the transition point method and found to be *the stable salt from the boiling point of its saturated solution in liquid ammonia to +20° C. at atmospheric pressure.* Under 2 cm. pressure, the hexammine bromide dissociates at +54.9° C.[3]

VI. Copper Iodide.

For these experiments, the compound $(CuI_2)_3.10NH_3$, described by Kohlschütter,[4] served as the basis. The general description of its preparation given by him is less satisfactory than the following explicit directions: Dissolve 30 grams pentahydrated copper sulphate in 100 cc. water and add 40 cc. ammonia water (sp. gr. 0.9). Dissolve 43 grams potassium iodide in 40 cc. water and add this to the ammoniacal sulphate solution. Then pass ammonia gas into the mixed solution, cooling gradually, until the solution is saturated with the gas at 0° C. In this way, most of the copper separates as the compound $CuI_2.4NH_3.H_2O$.[5] Collect this compound on a perforated porcelain plate with the aid of a filter pump, pressing it with a pestle to free it rapidly from the mother liquor. Place in a desiccator over freshly broken

[1] The temperature of the bath was 56° C.
[2] Rose: *Loc. cit.*
[3] Temperature of bath, +62° C.
[4] Ber. d. chem. Ges., **37**, 1137 (1904).
[5] Berthemot: Jour. d. Pharm., **15**, 445. Rammelsberg: Pogg. Ann., **48**, 162 (1839). Kohlschütter: *Loc. cit.*

potassium hydroxide until dry. Prepare a water solution of this compound approximately saturated at ordinary temperatures and rapidly add 50 cc. of it, with constant stirring, to 38 cc. of water containing 50 grams potassium iodide. Filter this solution after half an hour to remove any tetrammine salt that may have separated. After 24 hours collect the compound $(CuI_2)_3.10NH_3$ and dry between filter paper and over potassium hydroxide

It is not essential that the tetrammine salt should be dried, but if the saturated solution is prepared from the salt after taking it from the funnel there is enough ammonia present to delay the separation of the compound $(CuI_2)_3.10NH_3$ for 72 or more hours.

Prepared under these conditions, the compound can be identified by its appearance. It resembles copper bromide or iodide very closely in color and general aspect. Its streak is brown, like that of limonite.

When finely ground it is acted upon by ammonia gas immediately, the brown color changing rapidly to green and later to blue. It is freely soluble in liquid ammonia, the solution yielding beautiful deep-blue crystals upon evaporation. These crystals are very stable as long as moisture is excluded, but they decompose with great rapidity when brought into the air and leave a brown to black residue. The following results were obtained in its analysis:

Weight taken for analysis Gram.	Volume of acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $CuI_2.6NH_3$.
0.4803	34.06	23.58	24.38
0.3699	26.18	23.54	.. ..
0.4833	35.09	24.15	.....

When treated with liquid ammonia and examined by the transition point method *this hexammine iodide proved to be the stable compound at all temperatures between the boiling point of its saturated solution in liquid ammonia and +20° C. at atmospheric pressure.* At 2 cm., this hexammine salt dissociates at +67°.4 C.[1]

[1] Temperature of bath, +76° C.

Although the chloride, bromide, and iodide combine with 6 ammonia groups, two other salts of monobasic acids that had received considerable attention, namely, the acetate and sulphocyanate, required further study before a generalization could be thought of. The diammine acetate and the tetrammine sulphocyanate were the most complex salts known in these cases.

VII. Copper Acetate.

The diammine acetate has been described by Foerster[1] and later by T. W. Richards and Oenslager.[2] The following method of preparation requires much less manipulation and gives a considerably better yield than any that had been given: Saturate 150 cc. 95 per cent alcohol with dry ammonia, cooling to keep it approximately at the temperature of the room. Add 20 grams finely powdered green monohydrated copper acetate, and pass ammonia gas into the solution for about ten minutes longer, allowing the solution to warm up in the meanwhile. Filter and set aside, exposed to the air, for about 15 hours. This supersaturated solution deposits, in this time, only a few crystals about its upper surface. Filter rapidly and shake. The diammine acetate separates immediately. Dry the salt between filter paper in a press and preserve in a desiccator over potassium hydroxide. The product was identified by the following analyses:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia.	Percentage ammonia found.	Percentage calculated for $Cu(OOCCH_3)_2.2NH_3$.
0.3581	17.07	15.86	15.82
0.2236	10.63	15.82	.....

The diammine salt increases in weight in ammonia gas, as found by Foerster, but the increase is more than the 12.8 per cent stated by him. The gain in weight of 0.6274 gram of the diammine acetate when kept in dry ammonia gas at the temperature of the laboratory and one atmosphere pressure is given in the following table. Column III. is especially significant in connection with Foerster's statement.

[1] Ber. d. Chem. Ges., **25**, 3416 (1892).
[2] This Journal, **17**, 305 (1895).

Time of exposure. Hours.	Total gain in weight. Gram.	Gain per hour. Gram.	Percentage gain in weight.	Percentage calculated for formation of $Cu(OOCCH_3)_2.4NH_3$.
24	0.0575	0.0024	9.17	15.82
45	0.0793	0.0010	12.65	.....
75	0.0874	0.0003	13.93	.....
144	0.0895	0.0003	14.26	.....

When liquid ammonia is drawn upon it the diammine acetate changes in color at once. If the ammonia is allowed to evaporate at atmospheric pressure while the substance warms up to the temperature of the laboratory, the addition product is the same tetrammine salt that is chiefly formed in the above experiment in ammonia gas. In the following analyses, 0.8607 gram of the addition product was weighed after it had been dropped into an excess of dilute sulphuric acid to prevent loss of ammonia, and the acid was then diluted to the mark on the neck of the 200 cc. measuring flask in which the substance had been weighed.

Volume solution taken for analysis. cc.	Volume acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $Cu(OOCCH_3)_2.4NH_3$.
48.14	16.99	27.27	27.31
48.10	17.03	27.36	.....
	Weight Cu_2S found. Gram.	Percentage of copper found.	
31.60	0.0434	25.50	25.45

These results furnish satisfactory proof of the existence of the tetrammine salt, $Cu(OOCCH_3)_2.4NH_3$, a conclusion which Foerster had drawn from his observation that the diammine salt increased 12.8 per cent by weight in ammonia gas. *The transition point method showed the existence of a yet higher acetate, i. e., one containing more than 4 ammonia groups per molecule, but it was not possible, with the facilities at hand, to establish its formula. It has a tension of 1 atmosphere when it dissociates at about —22° C.*

VIII. Copper Sulphocyanate.

The preparation of the diammine and tetrammine sulphocyanates has been discussed sufficiently in a previous paper.[1]

[1] This series, III.

Either can be prepared pure without difficulty. The tetrammine salt used in these experiments was recrystallized twice from a very strong solution of ammonia in water by drawing a rapid stream of air through the solution. It deposited in the form of very small crystals. The diammine salt was obtained by exposing the mother liquors of the tetrammine salt to the air.

In the presence of water the direction of the reaction

$$Cu(SCN)_2.2NH_3 + 2NH_3 \rightleftharpoons Cu(SCN)_2.4NH_3$$

depends upon the relative concentrations of copper sulphocyanate, ammonia, and water.[1] When there is no water present it depends upon the pressure of ammonia gas. At 1 atmosphere and ordinary temperatures, the tetrammine salt is formed. The diammine salt, under these conditions, attained a practically constant weight in about 18 hours.

Weight diammine salt taken. Gram.	Gain in weight. Gram.	Percentage gain in weight.	Percentage calculated for formation of $Cu(OOCCH_3)_2.4NH_3$.
0.2891	0.0452	15.62	15.95
0.5520	0.0863	15.63	" "

The transition point method showed the existence of a higher sulphocyanate dissociating at atmospheric pressure at about $+10°$ C. It was impossible to weigh it for analysis by any of the ordinary methods. Accordingly, small pieces of apparatus, resembling distilling flasks in general form, were made from soft glass tubing. The side tubes were bent down at right angles and both the neck and side tube were constricted so that they could be sealed off quickly before the blast lamp. The experiments consisted in determining the increase in weight of the whole apparatus when liquid ammonia had been drawn upon a known weight of pure tetrammine salt contained in the bulb and the excess allowed to boil off. The whole apparatus, with the exception of the side tube, whose end dipped just beneath the surface of mercury, was kept surrounded with ice. The neck was sealed off immediately after the ammonia was introduced; and the side tube, when no more bubbles passed through the mercury.

[1] Horn: *Loc. cit.*

The total weight of each piece of apparatus ranged from 11 to 14 grams. The results follow:

Weight tetrammine salt taken. Gram.	Gain in weight. Gram.	Percentage gain in weight.	Percentage calculated for formation of $Cu(SCN)_2.5NH_3$.
0.4367	0.0274	6.27	6.88
0.3786	0.0248	6.54	....
0.4332	0.0298	6.88	....

Evidently the composition of this new salt is represented by the formula $Cu(SCN)_2.5NH_3$. Its color is bluer and less purple than that of the tetrammine salt. It crystallizes in scales from boiling liquid ammonia, in which it is freely soluble. It is of special interest as the only known anhydrous *pentammine* copper salt of a *monobasic* acid, whether the addendum be ammonia or any of the other bases thus far shown to combine with copper salts. Its existence proves clearly and for the first time that the pentammine type is not conditioned by the presence of a dibasic acid residue.

Diammine copper sulphocyanate dissolves freely in pyridine, as in liquid ammonia, and gives a dark olive-green solution from which emerald-green crystals gradually separate. They lose pyridine rapidly but can be quickly dried between filter paper and weighed for analysis without sensible decomposition. The following results were obtained in analyses for copper.

Weight taken for analysis. Gram.	Weight Cu_2S found.	Percentage copper found.	Percentage calculated for $Cu(SCN)_2.4C_5H_5N$.
0.2874	0.0456	12.66	12.82
0.2474	0.0392	12.65	.....

The composition of the salt can probably be represented by the formula $Cu(SCN)_2.4C_5H_5N$.

IX. Copper Acetoiodide and Acetobromide.

Some of the mixed cuprammonium compounds described by T. W. Richards and his students offered exceptional opportunities in efforts to determine the effect of the acid residue. Since copper acetate can take up but 4 ammonia groups at ordinary temperatures, and the iodide or bromide 6, it seemed especially interesting to determine whether or not the aceto-

iodide and acetobromide would combine with five, *i. e.*, the average of the four of the acetate and the six of the halide.

The compound $Cu\begin{matrix}I \\ C_2H_3O_2.3NH_3\end{matrix}$[1] was prepared as follows: 12 grams of the salt $Cu(C_2H_3O_2)_2.H_2O$ were dissolved in 50 cc. ammonia water (sp. gr. 0.9), the solution cooled, and then 30 cc. 57 per cent acetic acid, 6 grams ammonium iodide, and 50 cc. 95 per cent alcohol added separately in the order given. After being heated on the water bath the mixture gave a clear, deep-blue solution which was filtered and set aside exposed to the air. The crystals which separated were dried between filter paper and then over potassium hydroxide. They were analyzed for identification, with the following results:

Weight taken for analysis. Gram.	Volume acid neutralized by ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $CuIC_2H_3O_2.3NH_3$.
0.2688	13.85	17.14	17.03
0.4257	21.52	16.81	.....

When the substance was treated with liquid ammonia an intensely colored solution and a deep-blue solid deposit were obtained. The solid was separated and the excess of liquid ammonia allowed to evaporate from it at atmospheric pressure while it warmed up to room temperature. The analysis was conducted as in the case of the acetate.

1.0970 grams were weighed in sulphuric acid and diluted to 100 cc. Portions of this solution were analyzed:

Volume solution taken for analysis. cc.	Volume acid neutralized by the ammonia.	Percentage of ammonia found.	Percentage calculated for $Cu(C_2H_3O_2)_2.4NH_3$.
24.03	21.64	27.30	27.31
23.13	20.83	27.30	.....
	Weight of Cu_2S found. Gram.	Percentage copper found.	
9.47	0.0333	25.57	25.45
8.65	0.0302	25.41	.....

Instead of being an addition product of the acetoiodide, this compound is evidently the tetrammine acetate previously described in this paper. The hexammine iodide is very soluble in liquid ammonia while the acetate is only slightly

[1] Richards and Oenslager: THIS JOURNAL, 17, 298 (1895).

soluble, imparting but a faint color to the solvent. Apparently the liquid ammonia resolves the mixed molecule into its constituents as a result of this great difference in their solubility.

The acetobromide, $Cu\begin{matrix}Br \\ \diagup \\ \diagdown \\ C_2H_3O_2.2NH_3\end{matrix}$[1], was prepared as follows: Ammonia water (sp. gr. 0.9) was titrated against glacial acetic acid, and 10 cc. found to be equivalent to 7.41 cc. of the acid. Five grams anhydrous copper bromide (Kahlbaum) were treated with 10 cc. of the ammonia water, 7.3 cc. of the acetic acid, and 70 cc. 95 per cent alcohol in the order given. The resulting mixtures was heated on a water bath until the brown deposit that had formed was dissolved. The solution was then cooled under the tap to complete the separation of blue crystals that had begun before the heating. When analyzed for identification, the following results were obtained:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia.	Percentage of ammonia found.	Percentage calculated for $CuBrC_2H_3O_2.2NH_3$.
0.5048	21.85	14.40	14.42
0.4000	17.29	14.38	.....

When treated with liquid ammonia, a colored solution and a deep-blue solid were obtained. Two separate samples, A and B, of the solid were analyzed. 0.4438 gram A and 0.9295 gram B were weighed in sulphuric acid and the solutions diluted to 100 cc. The results follow:

	Volume of solution taken for analysis. cc.	Volume acid neutralized by the ammonia. cc.	Percentage ammonia found.
A	23.86	9.08	28.53
	23.76	9.07	28.61
B	23.63	18.87	28.58
	17.58	14.01	28.52
		Weight Cu_2S found. Gram.	Percentage of copper found.
A	14.45	0.0189	23.56
	14.76	0.0189	23.03
B	8.63	0.0228	22.90
	8.79	0.0234	22.78

[1] Richards and Shaw: THIS JOURNAL, 15, 644 (1893).

Hexammine copper bromide is much less soluble in liquid ammonia than the iodide, though considerably more soluble than the acetate. The composition of the solid indicates that it contained both salts. It is not possible, at present, to say finally whether in this solid I had a mixture or a compound. The ammonia determinations are to be given greater weight than those of copper in all cases where a halogen is present, and they indicate a solid of the same composition in the two cases. A mixture or compound of 1 mol. $CuBr_2.6NH_3$ and 3 mol. $Cu(C_2H_3O_2)_2.4NH_3$ requires 28.55 per cent ammonia and 23.65 per cent copper.

These experiments show that in all probability the mixed cuprammonium salts are quite different from the simple ones and are not to be regarded as substitution products derived from the latter. A study of the conditions under which these unique compounds exist in stable equilibrium in the presence of their components only is very desirable. They exist in hydrated as well as in anhydrous forms and, in three out of the nine known cases, exhibit the *triammine* type. The only other authentic case of this type among copper ammonia compounds is the cyanide, $Cu_3(CN)_4.3NH_3$,[1] in which, it will be noticed, the molecule is also a mixed one.

The study of salts of dibasic acids was next followed somewhat further, the dithionate, the orthophthalate, and the carbonate being used.

X. Copper Dithionate.

The anhydrous tetrammine dithionate described by Heeren[2] was prepared as follows: Pure manganese dioxide was obtained by heating the compound $Mn(NO_3)_2.6H_2O$ at $+165°$ C. for 8 hours. After the dioxide had been washed, it was placed with water in a large Peligot tube and sulphur dioxide passed through the water until the manganese dioxide had dissolved. The manganese and sulphuric acid were then removed by using a very slight excess of barium hydroxide, and the solution of barium dithionate was added to a satu-

[1] Schmidt: Jahres. d. Chem., **1898**, 1, 783. Malmberg: *Ibid.* Treadwell and Girsewald: Z. anorg. Chem., **39**, 84 (1904).

[2] Pogg. Ann., **7**, 189 (1826).

rated solution of copper sulphate until barium sulphate was no longer precipitated. After filtering, the solution was evaporated to a small volume on a water bath and placed in a desiccator over sulphuric acid. The dithionate of copper gradually crystallized out. The crystals were dried between filter paper. Eight grams of the crystals were dissolved in 12 cc. water and treated gradually with 35 cc. ammonia water (sp. gr. 0.9). The cuprammonium dithionate is not very soluble under these conditions and separates in thin flat plates. It can be recrystallized from ammonia water and dried over potassium hydroxide. When analyzed for identification, the following results were obtained:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia. cc.	Percentage ammonia found.	Percentage calculated for $CuS_2O_6.4NH_3$.
0.4859	33.90	23.21	23.38
0.3916	27.44	23.31	.....

The tetrammine dithionate is blue with a reddish cast. Its streak is lilac. When treated with liquid ammonia it acquires a blue color free from reddish shades and yields a product that gave the following results upon analysis. The first preparation was weighed as such while the second was dropped into sulphuric acid and weighed and the solution diluted to 100 cc.

I.	Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $(CuS_2O_6)_2.9NH_3$.
	0.2530	19.13	25.15	25.55
		Weight Cu_2S found. Gram.	Percentage of copper found.	
	0.3318	0.0877	21.11	21.16
	0.3237	0.0860	21.21	.....
II.	Volume of solution taken for analysis. cc.	Volume acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated.
	23.79	15.17	25.14	25.55
	23.82	15.45	25.56	.....
		Weight Cu_2S found. Gram.	Percentage of copper found.	
	9.06	0.0205	21.37	21.16
	10.27	0.0232	21.37	.....

The formula $CuS_2O_6.4\frac{1}{2}NH_3$, or, more properly, $(CuS_2O_6)_2.9NH_3$, indicated by the analysis is not a simple one. It gives evidence of a condition within the molecule not unlike that which has been met with in the compounds $(CuBr_2)_3.10NH_3$ and $(CuI_2)_3.10NH_3$. This dithionate is very unstable at ordinary temperatures and dissociates with great rapidity in the air, yielding a lilac product that was shown, by the following analysis, to be the original tetrammine salt.

Weight taken for analysis. Gram.	Weight Cu_2S found. Gram.	Percentage copper found.	Percentage calculated for $CuS_2O_6.4NH_3$.
0.1452	0.0397	21.82	21.78
0.1731	0.0472	21.77	.....

The transition point method indicated that no higher compound than $(CuS_2O_6)_2.9NH_3$ is formed at any temperature between that of the room and that of boiling liquid ammonia. The dithionate is insoluble in liquid ammonia.

XI. Copper Orthophthalate.

Monohydrated copper orthophthalate was prepared as follows: 5 grams phthalic anhydride were dissolved in 1 liter of water and the solution boiled with 2.5 grams copper carbonate (Kahlbaum) approximating closely to the formula $Cu(OH)_2.CuCO_3$. The carbonate contained 56.2 per cent copper and 18.8 per cent carbon dioxide while the formula requires 57.5 per cent copper and 19.9 per cent carbon dioxide. The solution of copper orthophthalate, after boiling, was filtered and evaporated to 350 cc. on a water bath. After it had cooled, the copper salt, which separated, was collected and dried in the air. It was then dehydrated by heating to constant weight at +160° C. in an air bath, as directed by Hermann.[1] The blue salt changes to a deep olive-green in this process and loses about 7.2 per cent, the calculated amount of water being 7.3 per cent. Placed in ammonia gas it rapidly changes to a very dark blue, increasing about 33 per cent in weight. The formation of the compound $(Cu(OOC)_2CuH_4)_3.9NH_3$ requires 33.73 per cent gain.

When treated with liquid ammonia the same dark-blue

[1] Ann. Chem. (Liebig), **181**, 78 (1869).

color is developed and the product, when analyzed, gives results indicating this same formula.

0.7305 gram of the dark-blue product was weighed in sulphuric acid and the solution diluted to 100 cc. This solution was analyzed, with the following results:

Volume of solution taken for analysis. cc.	Volume acid neutralized by the ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $[Cu(OOC)_2C_6H_4]_2.9NH_3$.
23.09	12.67	24.99	25.22
24.33	13.38	25.04	.....
	Weight Cu_2S found. Gram.	Percentage copper found.	
9.30	0.0177	20.83	20.89
8.20	0.0157	20.87	.....

This orthophthalate, therefore, has a formula analogous to that of the highest dithionate, $[Cu(OOC)_2C_6H_4]_2.9NH_3$.

The transition point method, when applied to this substance, indicated the existence of a higher orthophthalate with a tension of 1 atmosphere when dissociating at about —8° C.

XII. Copper Carbonate.

The diammine copper carbonate described by Favre[1] was prepared as follows: 50 cc. of a cold saturated solution of the solid "C. P. ammonium carbonate" of commerce was treated with 10 cc. ammonia water (sp. gr. 0.9) and then saturated with the same copper carbonate used in the preparation of the orthophthalate. About 6 grams copper carbonate were required. After the solution was filtered, 95 per cent alcohol was added slowly while the mixture was thoroughly shaken. The diammine salt separated in fine crystals that were pressed between filter papers and dried over potassium hydroxide. The following analysis served to identify it:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia.	Percentage ammonia found.	Percentage calculated for $CuCO_3.2NH_3$.
0.7812	49.94	21.26	21.64
0.7469	48.22	21.47	.....
	Weight Cu_2S found. Gram.	Percentage copper found.	
0.2917	0.1471	40.27	40.42
0.1793	0.0907	40.39	.....

[1] Ann. Chim. Phys. [3], 10, 116.

This diammine salt behaves as a *saturated* compound toward ammonia. Liquid ammonia may be boiled off from it for a period of at least one hour and the salt remains entirely unchanged. This case, with others, will be discussed in the next paper in this series.

Although other cuprammonium carbonates have been isolated in the course of this investigation, I have not yet succeeded in preparing any other anhydrous salt.

XIII. Copper Nitrate.

The tetrammine nitrate described by Kane[1] was prepared as follows: 10 grams crystallized hexahydrated copper nitrate were dissolved in 8 cc. water, and 25 cc. ammonia water (sp. gr. 0.9) then added. The mixture was heated until a clear solution was obtained and this was then shaken continuously and cooled in a stream of tap water. The crystals were dried over potassium hydroxide after they had been pressed between filter papers. When it was analyzed the following results were obtained:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia. cc	Percentage ammonia found.	Percentage calculated for $Cu(NO_3)_2.4NH_3$.
0.5147	40.96	26.47	26.67
0.5425	41.60	26.43	.....
0.5522	42.27	26.39	.....
	Weight Cu_2S found. Gram.	Percentage copper found.	
0.3223	0.1002	24.83	24.85
0.3203	0.1002	24.98	.....

This nitrate is freely soluble in liquid ammonia and forms a more complex compound that has a pressure of 1 atmosphere when dissociating at about $+15°$ C. This higher nitrate, like the pentammine sulphocyanate, cannot be analyzed by the ordinary methods. At first, bulbs were blown on test tubes and these were weighed empty and then with the tetrammine nitrate. Liquid ammonia was then drawn upon the salt, which dissolved completely. The test tubes were fitted with rubber stoppers carrying delivery tubes which were

[1] Ann. Chim. Phys. [2], **73**, 225, 337.

immersed in mercury to a depth of 20 cm. After all of the ammonia had boiled away, as indicated by the absence of bubbles rising through the mercury, the delivery tubes were raised almost to the surface of the mercury and the test tubes sealed off at constrictions made in them when the bulbs were blown. The bulbs and the parts of the test tubes removed in sealing were later weighed, with the following results:

Weight tetrammine salt taken Gram.	Gain in weight found. Gram.	Percentage gain in weight.	Percentage calculated for formation of $[Cu(NO_3)_2]_4.23NH_3$.
0.4618	0.0514	11.14	11.67
0.3952	0.0445	11.25	.....

This highest nitrate, $Cu(NO_3)_2.5\frac{3}{4}NH_3$, or, more properly, $[Cu(NO_3)_2]_4.23NH_3$, has an almost sapphire-blue color whereas the tetrammine salt formed by its decomposition has a lilac color. In these bulbs there was a slight amount of lilac salt at places on the edges of the blue crystals. Accordingly apparatus of the kind used in determining the composition of the pentammine sulphocyanate was brought into use here. The excess of liquid ammonia was allowed to boil off at 1 atmosphere and 0° C. in these experiments, and the following results were obtained:

Weight tetrammine salt taken. Gram.	Gain in weight found. Gram.	Percentage gain in weight.	Percentage calculated for formation of $[Cu(NO_3)_2]_4.23NH_3$.
0.5238	0.0632	12.06	11.67
0.5131	0.0620	12.08	....
0.4706	0.0567	12.05	....

In these bulbs there was no other color to be seen but the sapphire-blue color. The results are slightly higher than required by the formula, but this may have been due to the retention of small amounts of mother liquor by the crystals. The total amount of ammonia in these specimens amounted to 34.56 per cent, 34.57 per cent, and 34.61 per cent, respectively, and the formula requires 34.33 per cent. The tetrammine nitrate is soluble in about its own weight of liquid ammonia and the sapphire-blue compound separates in thick plates. The apparatus was sealed when no more bubbles escaped through the mercury for five minutes, but further

small amounts of occluded ammonia might have escaped had more time been allowed. All attempts to analyze the compound in the usual way yielded results that were not concordant, for the substance loses ammonia with extreme rapidity when exposed to the air.

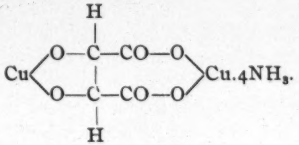
Examined by the transition point method, this system was found to be divariant from the time the liquid ammonia had boiled off until the lilac tetrammine salt appeared. It then became monovariant. It exhibited this same behavior from —41.°4 C. at 2.2 cm. pressure to +50.°3 C. at 234.7 cm. This is positive proof that the sapphire-blue substance is a definite compound. For if it were a mixture of two compounds, neither of which was the tetrammine salt, the system could never be divariant, but would be monovariant from the time the liquid ammonia had boiled off until the lilac salt appeared, and then it would become invariant. And if it were a mixture of two compounds, one of which was the tetrammine salt, the system would be monovariant throughout and the appearance of the lilac salt in visible quantity would in no way affect its degree of variability. The fact that the sapphire-blue substance crystallizes from complete solution in liquid ammonia makes the assumption that it is a product of incomplete addition very improbable. So far as the experiments go, they show that the sapphire-blue substance is a definite addition product of the tetrammine nitrate and that its composition is correctly represented by the formula, $Cu(NO_3)_2.5\frac{3}{4}NH_3$, or $[Cu(NO_3)_2]_4.23NH_3$.

Some progress had been made in similar studies of the chlorate, bromate, and perchlorate, but difficulties met with in the analysis of these compounds made it impossible to complete experiments before the work had to be given up.

A new tartrate that was prepared in the course of experiments directed toward obtaining an anhydrous diammine tartrate should perhaps be described in this place. It was formed when precipitated copper tartrate was treated with ammonia water (sp. gr. 0.9), and the mixture heated. The tartrate appeared to dissolve and crystallize out again in the form of the compound $Cu_2C_4H_2O_6.4NH_3.2H_2O$. The analysis resulted as follows:

Weight taken for analysis. Gram.	Volume acid neutralized by the ammonia. cc.	Percentage ammonia found.	Percentage calculated for $Cu_2C_4H_2O_6.4NH_3.2H_2O$.
0.3661	18.28	18.12	18.08
0.3919	19.63	18.17	....
	Weight Cu_2S found. Gram.	Percentage copper found.	
0.4044	0.1713	33.82	33.67
0.3479	0.1470	33.75	....

This is evidently the hydrated form of the interesting tartrate described by Bullheimer and Seitz[1] and which is said to be formed in Fehling's solution, *i. e.*,



The hydroxyl hydrogen, as well as the carboxyl hydrogen, is replaced by copper or cuprammonium groups.

This tartrate resembles the crystallized anhydrous diammine oxalate very closely in color and in other respects.

XIV. Solubilities in Liquid Ammonia.

In the following list, the salts imparting no color to liquid ammonia are classed as insoluble, those imparting a faint color as slightly soluble, those an intense color as very soluble, and the rest as moderately soluble. The slightly soluble and moderately soluble salts are arranged from top to bottom in the order of increasing solubility.

Insoluble.	Slightly soluble.	Very soluble.
Sulphate	Orthophthalate	Nitrate
Oxalate	Acetate	Iodide
Succinate		Sulphocyanate
Dithionate		
Carbonate		
Chloride		

Moderately soluble.

Acetobromide, with decomposition
Bromide
Acetoiodide, with decomposition

[1] Ber. d. chem. Ges., **32**, 2347 (1899).

XV. Color.

In the course of the work upon which this series of papers has been based, I have prepared about 28 crystallized cuprammonium compounds and about half as many amorphous or pseudomorphic cuprammonium compounds of definite composition. Upon this basis it seems proper to make some statements as to the colors of these compounds. The general impression that all the salts containing 4 ammonia groups are of the same color is, in one sense, erroneous. The deep-blue color that has become familiar through the sulphate, $CuSO_4.4NH_3.H_2O$, is modified more or less by red or purple in every case. Each crystallized tetrammine salt can readily be distinguished by its color from any other one that is brought beside it, so far as I have been able to observe. Side by side comparison is not even required in some cases; for example, the tetrammine dithionate is so much redder than the tetrammine sulphate, and the tetrammine perchlorate[1] is so much less red than the sulphate that confusion would be impossible. The deep-blue colors of solutions of different tetrammine salts can likewise often be distinguished, in some cases without a side by side comparison.

If all of the red or purple modifications of the deep-blue color referred to are regarded as identical, this color is not characteristic of compounds containing 4 ammonia groups. The *pentammine* oxalate and the *diammine* acetate, for example, resemble the *tetrammine* sulphate more closely than does the *tetrammine* dithionate or perchlorate.

These statements concerning the solids refer to the reflected colors, but there are also differences in the body colors, or streaks.

Perhaps the greatest differences in color among salts of any one degree of complexity are found in the *diammine* salts. The dihydrated diammine succinate no more resembles in color the corresponding oxalate than potassium permanganate resembles crystallized copper nitrate. Among the anhydrous diammine salts, the oxalate is a brilliant sapphire, the carbonate a rich, deep, pure blue, the sulphocyanate a faded

[1] Ann. Chem. (Liebig), 121, 355 (1862).

grayish-blue, and the acetate has a color resembling ordinary cuprammonium sulphate (tetrammine). The hydrated tartrate described above, in which the ratio $Cu:NH_3:H_2O$ is 1:2:1, resembles the anhydrous diammine oxalate so closely that a side by side comparison is necessary in order to distinguish them, while the ferrocyanide,[1] in which the same ratio, 1:2, occurs, is chocolate-brown. The anhydrous diammine acetate and the anhydrous diammine acetobromide differ almost as much in color as the familiar monohydrated tetrammine sulphate differs from ordinary pentahydrated copper sulphate.

It is a necessary conclusion, from the data at hand, that the color depends not only on the number of ammonia groups present but also on the acid residue. Because the color of all the hexammine, pentammine, and tetrammine salts that have been described is a more or less red modification of the same deep-blue color, one would infer that the effect of the ammonia upon the color overweighs that of the acid residue when the number of ammonia groups per copper atom is as great as 4. Because the diammine salts, on the contrary, exhibit a diversity of color, one would infer that when the number of ammonia groups per copper atom is not greater than 2, the effect of the ammonia is overweighed by that of the acid residue.

The effect of the acid residue upon the color, however, is not dependent upon the chemical nature alone of the acid, for one and the same acid may combine with the copper and ammonia in precisely the same ratio and yet yield products that are not identical in color. In the one case of this kind that I have met with, there is a difference in the molecular volumes of the two substances, which may mean a difference in the volume occupied by the acid residue, and this may be associated in some way with the difference in color.

It is scarcely conceivable that water molecules, when present, are without some effect upon the color, but I know of no cases where this is appreciable except in diammine salts of dibasic acids, and such cases cannot safely be used as data

[1] Messner: Z. anorg. Chem., 8, 368.

now because we do not know whether or not isomerization occurs when such molecules are hydrated or dehydrated.

XVI. The Acid Residues and the Formation of Complexes.

When the copper salts are arranged according to their valence, at atmospheric pressure and between $-30°$ and $+9°$, toward ammonia, the following table is obtained:

	Valence toward ammonia.
CuI_2, $CuBr_2$, $CuCl_2$	6
$Cu(NO_3)_2$	5¾
$CuSO_4$, $Cu(OOC)_2C_2H_4$, $Cu(OOC)_2$, $Cu(SCN)_2$	5
CuS_2O_6	4½
$Cu(OOCCH_3)_2$	4 (between $-22°$ and $+10°$).

The hexammine salts dissociate at 2 cm. pressure at the following temperatures: Iodide, $+67°.4$; bromide, $+54°.9$; chloride, $+46°.7$. Therefore the iodide is the most stable, and the chloride the least stable.

The pentammine salts, when placed over sulphuric acid at the temperature of the laboratory, lose 1 molecule of ammonia in approximately the following lengths of time: Sulphate, 1 week; succinate, 1 day; oxalate, 1.5 hours. The pentammine sulphocyanate is less stable than these, for it dissociates at atmospheric pressure at about $+10°$, while they all dissociate at temperatures above $+20°$.

The copper salts that form hexammine and pentammine derivatives have been so arranged in the above table that the order indicates the relative stabilities of their ammonia compounds, as determined by the facts just mentioned.

This order into which the copper salts fall is unique among the experimental facts in the chemistry of metal-ammonia compounds. It is likely susceptible of more than one interpretation, and the following one is suggested merely because it seems as simple as possible. The equivocal meaning of the terms *affinity* and *valence* renders difficult any attempt

at explaining this order and the situation does not seem to me to be relieved at all by adopting any of the modified terms derived from these two that have been proposed more or less recently.

Since the complexity and stability of the compounds have been determined under the same conditions of temperature and pressure in systems that differ from each other *only* in the chemical nature of the acid residue, it follows that the order of the salts of the acids given above must be the order of the acid residues themselves in their influence on complexity and stability.

If the idea of a force of attraction is adopted in dealing with these facts, although it may be questioned whether the existence of such a force acting through space from particle to particle has ever been demonstrated, the molecule of a copper salt exists as a result of the attractions between the copper atom and the acid residue. The attraction exhibited by the molecule of copper salt, when once formed, toward ammonia may be regarded as the resultant of the attractions between the copper atom and the acid residue. Whether the attraction exhibited by a copper atom toward an acid residue is assumed to be constant, or to depend upon the acid residue toward which it is exerted, the values of the resultants are proportional to the attractions of the acid residues. The acid residues, then, stand in the same order, with respect to their attractions toward copper, as do their salts in the table above. Whether such an attraction is *affinity* or not depends upon the definition of *affinity* adopted by the reader.

Whether or not it is assumed that this is *affinity*, it is interesting to compare the order with the results obtained by Ostwald in his studies on affinity. The acids are arranged in column I. of the following table according to the results with cuprammonium salts, in II. according to Ostwald's studies on the solution of calcium oxalate in mixed acids, in III. according to his work on the velocity of the hydrolysis of acetamide, in IV. according to the results obtained by him in the study on the saponification of methyl acetate, and in V. according to his investigation on the inversion of cane sugar.

I. −30° to +9°.	II.	III.	IV.
HI	HNO_3	HCl	HCl
HBr	HCl	HBr	HBr
HCl	HBr		HI
HNO_3		HNO_3	HNO_3
H_2SO_4		H_2SO_4	H_2SO_4
$C_4H_6O_4$	$C_4H_6O_4$	$C_2H_2O_4$	$C_2H_2O_4$
$C_2H_2O_4$		$C_4H_6O_4$	$C_4H_6O_4$
HSCN			
$H_2S_2O_6$			
	$C_2H_4O_2$	$C_2H_4O_2$	$C_2H_4O_2$

V.	VI. −22° to +9°.	VII. +11° to +14°.	VIII. +16° to +20°.
HBr	HI	HI	HI
{ HCl }	HBr	HBr	HBr
{ HNO_3 }	HCl	HCl	HCl
	HNO_3	HNO_3	H_2SO_4
H_2SO_4	H_2SO_4	H_2SO_4	$C_4H_6O_4$
$C_2H_2O_4$	$C_4H_6O_4$	$C_4H_6O_4$	$C_2H_2O_4$
$C_4H_6O_4$	$C_2H_2O_4$	$C_2H_2O_4$	$H_2S_2O_6$
	HSCN	$H_2S_2O_6$	HNO_3
	$H_2S_2O_6$	HSCN	HSCN
$C_2H_4O_2$	$C_2H_4O_2$	$C_2H_4O_2$	$C_2H_4O_2$

Apparently side reactions or other influences in Ostwald's experiments are sufficiently significant to make the order of the acids having nearly equal "affinities," HCl, HBr, HI and HNO_3, doubtful when determined by the methods he used. One difference, however, appears in the orders as determined by Ostwald's methods and by the cuprammonium salts; in the first, oxalic acid precedes succinic acid, whereas in the second the reverse is true.

But the order determined by the cuprammonium salts depends upon the temperature, as is readily seen in columns VI., VII., and VIII. If the changes in the attraction of a molecule of copper salt for ammonia with changes in external conditions is examined by the aid of Fig. I., it appears that at constant capacity, *i. e.*, valence, the intensity of the attraction of any one copper salt for ammonia, if measured by the value of the pressure of ammonia required to prevent dissociation, increases as the temperature falls. At constant intensity, the capacity or valence also increases as the temperature falls, but by steps or leaps. A curve of dissociation tensions represents the physical conditions under which the valence of a molecule of copper salt changes to another value, and the path of the curve represents the rate of change, with temperature, of the intensity of the salt's attraction for ammonia at the higher of the two valences represented along the curve.

If the order of the acid residues secured in the way that has been followed above is the same as the order of their "affinities," the work done so far seems to indicate the necessity for some new conception in the comparison of affinities, analogous in a sense to Van der Waals' "Coincident states" in gases. For it is clear that without some such conception the order of relative affinity will depend upon an arbitrary choice of temperature, and, therefore, that any such order must be regarded as an arbitrary rather than a natural order.

Another assumption that may be made in dealing with the facts given above is that the affinity of a molecule of a copper salt for ammonia is independent of external conditions. Raising the temperature increases the kinetic energy of the constituents and increases the distance between the centers of

attraction, and thus reduces the intensity of the attractions that hold the compound together. This assumption brings into prominence the analogy between the change of dissociation tension with temperature in the case of a dissociating substance, and that of the vapor pressure with temperature in the case of a pure liquid. Such a method of consideration has this value, that it suggests the desirability of studying curves of dissociation tensions in order to see whether or not they end in "critical temperatures," beyond which the constituents could not be made to combine or to remain combined, no matter how great the pressure applied to them.

Whatever the value of these assumptions or any others that might be suggested, the experimental work will be pushed further. The corresponding order of the acid residues will be gotten by the study of other series of compounds, and similar studies will be made to determine the order in which the metallic atoms favor the formation of complexes. Curves of dissociation tensions will be studied from a more general point of view and through a much wider range of pressure.

ON THE VELOCITY CONSTANTS AND MECHANISM OF THE REACTIONS OF ALKYL HALIDES WITH URAZOLES AND URAZOLE SALTS.

[TWELFTH COMMUNICATION ON THE URAZOLES.[1]]

By S. F. Acree and G. H. Shadinger.

The following is a report of part of the work that is being carried on in this laboratory to learn the mechanism of the alkylation reactions involved when alkyl halides, sulphates, nitrates, potassium ethyl sulphate, and similar substances react with acids, bases, and salts, such as hydroxides, carbonates, nitrates, urazoles, and many others. We are studying the problem whether acids, bases, and salts enter into these reactions through their ions or molecules, or both. We are trying to learn how alkyl halides and other alkylating agents enter into these reactions.

[1] This Journal, **27**, 118; **31**, 185; **33**, 606; **37**, 71, 361; **38**, 1, 258. Ber. d. chem. Ges., **35**, 553; **36**, 3139; **37**, 184, 618.

Do the alkyl halides dissociate, as Bruyn and Steger[1] assumed, into alkyl and halide ions which then react with other substances present?

$$KOH + C_2H_5I \rightleftharpoons \overset{+}{K} + \overset{-}{O}H + \overset{+}{C_2H_5} + \overset{-}{I} \longrightarrow C_2H_5OH + \overset{+}{K} + \overset{-}{I}.$$

Do the alkyl halides unite with cations present, as Euler[2] assumed, and form complex cations which then react with other constituents of the solution?

$$KOH + C_2H_5I \rightleftharpoons \overset{+}{K} + \overset{-}{O}H + C_2H_5I \rightleftharpoons C_2H_5I.\overset{+}{K} + \overset{-}{O}H \longrightarrow$$

$$\begin{cases} (1)\ \overset{+}{C_2H_5} + \overset{-}{O}H + \overset{+}{K} + \overset{-}{I} \\ \text{or} \\ (2)\ C_2H_5I.\overset{+}{K} + \overset{-}{O}H \end{cases} \searrow \nearrow \quad C_2H_5OH + \overset{+}{K} + \overset{-}{I}.$$

Do alkyl halides, nitrates, sulphates, hydroxides, cyanides, etc., dissociate, as Nef[3] assumed, into an unsaturated olefine or methylene derivative and the corresponding acid or water, which then react with other substances and yield the alkyl derivatives as end products?

$$C_2H_5I + KOH \rightleftharpoons C_2H_4 + \overset{+}{H} + \overset{-}{I} + \overset{+}{K} + \overset{-}{O}H \longrightarrow$$

$$C_2H_4 + \overset{+}{K} + \overset{-}{I} + HOH \longrightarrow C_2H_5OH + \overset{+}{K} + \overset{-}{I}.$$

Do the alkyl halides unite with the anions and form complex anions which decompose into the corresponding ester and halide ions?

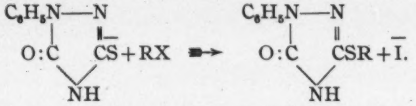
$$KOH + C_2H_5I \rightleftharpoons \overset{+}{K} + \overset{-}{O}H + C_2H_5I \longrightarrow$$

$$\overset{+}{K} + C_2H_5I.\overset{-}{O}H \longrightarrow \overset{+}{K} + \overset{-}{I} + C_2H_5OH.$$

In the present communication the problem is attacked by studying the action of alkyl halides on urazoles and salts of urazoles, hydroxides, thioacetates, etc. A series of alkyl iodides, bromides, and chlorides was used at different concentrations to learn the effect of change in concentration, and, at different temperatures to obtain the temperature coefficients. The thiourazoles and alkyl halides do not form ap-

[1] Rec. Trav. Chim., **18**, 311.
[2] Ber. d. chem. Ges., **39**, 2726.
[3] Ann. Chem. (Liebig), **298**, 202; **309**, 126; **310**, 316; **318**, 1, 137; **335**, 191.

preciable amounts of 2-alkylurazoles, as do the corresponding oxyurazoles,[1] but yield apparently only the 3-thioesters:



We investigated the question as to whether the anions of the urazoles, hydroxides, etc., or the undissociated substances, or both, react with the alkylating agents.

Various trials proved that the reaction goes to completion when the salt of the 1-phenyl-3-thiourazole and the alkyl halide (in slight excess) are allowed to react from two to four days. The reaction is then one of the second order, and if the anions react with the molecular alkyl halide the equation for the reaction velocity is

$$\frac{dx}{dt} = K_{trans} \times C_{anion} \times C_{alkyl\ halide} \qquad (1),$$

where K_{trans} is the reaction constant, C_{anion} is the concentration of the 1-phenyl-3-thiourazole anions, and $C_{alkyl\ halide}$ the concentration of the alkyl halide in gram molecules per liter. Under the conditions of the experiments the value of C_{anion} is always a definite fraction of the concentration of the urazole salt left in solution, and can be represented by $\alpha(A-x)$, in which α is the percentage of dissociation of the salt, A is the original concentration of the salt, and x the change in concentration of the salt. The differential equation then becomes

$$\frac{dx}{dt} = K_{trans}\,\alpha(A-x)(A-x) \text{ or } \frac{dx}{dt} = K(A-x)^2 \qquad (2)$$

when the alkyl halide and the urazole salt are originally present in the same concentration, A, and undergo the same change in concentration, x, in the time t. If the undissociated acid, base, or salt reacts with the molecular alkyl halide the equation for the reaction velocity is

$$\frac{dx}{dt} = K'_{trans} \times (1-\alpha)(A-x)(A-x) \text{ or } \frac{dx}{dt} = K'(A-x)^2 \qquad (3).$$

[1] Acree: THIS JOURNAL, 37, 71.

Since in these alkylation reactions the ionized and the undissociated portions of the urazole salt are always definite fractions of the concentration of the total urazole salt under given constant conditions, the concentration of the total salt can be substituted for the concentration of the ions or the undissociated salt in obtaining values for A, x, and $(A-x)$ in the equation $\frac{x}{t(A-x)} = AK$.

The equation therefore does not tell whether the total salt, the dissociated part, or the undissociated molecular part reacts. This question was settled by investigating the following problems:

1. The effect of adding a salt with a common ion and suppressing the ionization of the urazole salt.
2. The reaction velocity of different salts of phenylthiourazole. These different salts are dissociated to different extents and therefore have different reaction velocities.
3. The reaction velocity of the acid. This is less dissociated than the salt and so should have a smaller reaction velocity if it reacts through its ions.

The following problems also were studied:

4. The effect of change of concentration.
5. The temperature coefficient.
6. Ionization of the salts in 50 per cent alcohol.
7. How do the alkyl halides react?
8. The effect on the velocity constant produced by the change of the halogen in the alkyl halides.
9. The effect on the velocity constant produced by the change of the alkyl group in the alkyl halides.
10. Similar results in analogous reactions which are ionic.

Let us first discuss the conditions attending the reaction between sodium 1-phenyl-3-thiourazole and an alkyl halide. If we start with a solution which is 0.2 normal with respect to the sodium salt and the alkyl halide and let the reaction proceed for some time, the concentrations of the sodium salt and of the alkyl halides are constantly becoming smaller. We might at first thought expect an increase in the percentage of dissociation of the urazole salt, corresponding to such

dilution, and therefore expect an increase in the value of the velocity constant if the action is between the urazole ions and the alkyl halide, but a decrease in the value of the constant if the action is between the undissociated urazole salt and the alkyl halide. Such is not the case. Although the solution is 0.2 normal at the start, another salt, say sodium iodide, is formed, its concentration increasing as that of the sodium urazole salt decreases. The total number of gram molecules of the electrolyte present is a constant, 0.2, or the solution is always 0.2 normal with respect to the total amount of electrolyte. The work of Arrhenius,[1] Archibald,[2] and Jones[3] shows that the sodium urazole under these conditions can not change appreciably in percentage of dissociation. This follows from Arrhenius' theory that, since we have no accurate way of applying the mass law to such cases, the best way to approximate the ionization of two or more electrolytes in a solution is to assume that they share the solution between themselves in proportion to the concentration of each. For example, when half the sodium urazole is used up there is also an equal molecular amount of sodium halide formed. They then share the solvent equally and the amount of urazole left in half the solvent has the same concentration as before, 0.2 normal, and therefore is equally dissociated. This is true at any stage in the reaction, no matter what the concentration at the start.

1. As was said before, the value of the velocity constant obtained from any one set of experiments does not tell whether the action is molecular or ionic on the part of the urazole. After the addition of a certain number of molecules of sodium halide to the standard solution of sodium 1-phenyl-3-thiourazole, say 0.2 normal, the ionization of the urazole is no longer that of a 0.2 normal solution but corresponds to the new concentration which it must have in the presence of this added salt. For example, in 5 liters of solution contain 1 gram molecule of sodium 1-phenyl-3-thiourazole and 15 gram molecules of sodium iodide, the ionization of the

[1] Z. physik. Chem., **2**, 288; **31**, 206.
[2] Trans. Nov. Sco. Inst. Sci., **9**, 101.
[3] This Journal, **19**, 83; **22**, 5, 110; **25**, 349.

sodium urazole would be that of a 3.2 normal solution and not that of a 0.2 normal solution. The addition of the sodium iodide, then, causes a decrease in the ionization of the sodium urazole. If the reaction is between the urazole ions and the alkyl halide the reaction constant, expressed in the equation $\frac{dx}{dt} = K_{trans}\ \alpha(A-x)^2$, ought to decrease in direct proportion to the decrease in the percentage of dissociation of the sodium urazole. But if the action is between the undissociated molecules and the alkyl halide the reaction velocity, expressed in the equation $\frac{dx}{dt} = K'_{trans}(I-\alpha)(A-x)^2$, ought to increase with the increase in concentration of the undissociated molecular form. Of course these constants would be changed to some extent by the influence of the salts on the viscosity of the solution, by the hydration of the salts, both of which would have some effect on the velocity of the urazole ions, and *by any special catalytic action which the other salts might exert on the reaction.*

In all cases tried, a decrease in the value of the constant followed an addition of such an electrolyte to the urazole-alkyl halide solution. Apparently, then, the urazole ions react with the alkyl halide. When nonelectrolytes were added, however, there was no decrease but a slight increase, if anything, as is shown in Table II., experimental part. Electrolytes were added to solutions of sodium 1-phenyl-3-thiourazole and alkyl iodides, bromides, and chlorides, to barium 1-phenyl-3-thiourazole and ethyl iodide, to 1-phenyl-3-thiourazole and ethyl iodide, and to potassium hydroxide and ethyl iodide. *Since the constants decreased in all cases it seems that only the anions react with the alkyl halides.* See Tables II., VIII., X., XI., XII., XX., XXVII., XLI., and XLIII. in the experimental part.

Slator[1] got similar evidence that the action of sodium thiosulphate on the alkyl halides is ionic. He used ethyl bromacetate with that salt. The addition of a small quantity of silver nitrate decreased the activity of the thiosulphate

[1] J. Chem. Soc., **85**, 1286; **87**, 481. See also J. Chim. Phys., **4**, 565; **5**, 340.

because the silver nitrate rendered inactive that portion of the thiosulphate corresponding to the formation of $Na_3Ag(S_2O_3)_2$. The values of K so obtained approximated the value calculated for the sodium thiosulphate left unchanged. This result showed that the reactivity of trisodium silver thiosulphate is small compared with that of sodium thiosulphate and is negligible in the presence of a moderate excess of the latter salt.

When, however, an excess of silver nitrate was added the speed of reaction was only 0.05 of the original velocity. Slator thought that the complex salt dissociated thus:

$$Na_3Ag(S_2O_3)_2 \rightleftarrows 3\,\overset{+}{Na} + \overline{Ag(S_2O_3)_2},$$

and

$$\overline{Ag(S_2O_3)_2} \rightleftarrows \overline{AgS_2O_3} + \overline{S_2O_3}.$$

The ions $\overline{Ag(S_2O_3)_2}$ and $\overline{AgS_2O_3}$ and the corresponding undissociated salts either do not react at all or at least very slowly. The uncombined thiosulphate is represented by $\overline{S_2O_3}$ ions, and probably the reaction depends upon their presence. Therefore, the slow activity following the addition of silver nitrate is strong evidence in support of the view that the reaction is primarily connected with the $\overline{S_2O_3}$ ion.

2. If the reaction of the 1-phenyl-3-thiourazole salts is ionic and independent of the nature of the cation, various metallic salts of the 1-phenyl-3-thiourazole should give reaction constants, the values of which are directly proportional to the percentage of dissociation of those salts at the same concentration. The value of K_1 for 0.2 normal sodium phenyl-3-thiourazole and 0.2 normal ethyl iodide is 0.36. The value of K_1 for the barium salt in the same concentration is 0.32. See Tables IV., VIII., and IX. in the experimental part.

In 0.05 normal solutions sodium chloride is dissociated 87 per cent, and barium chloride 75 per cent. The velocity constants for all reactions of the sodium and barium salts of the 1-phenyl-3-thiourazole agree very well with this amount of dissociation, but the constant for magnesium 1-phenyl-3-

Temp.	Urazole.	Alkyl halide.	K_2.	
25°	Sodium 1-phenyl-3-thiourazole	Ethyl iodide	0.35	(Table V.)
25°	1-Phenyl-3-thiourazole	" "	0.192	(" XXXV.)
50°	Sodium 1-phenyl-3-thiourazole	" "	3.28	(" VI.)
50°	1-Phenyl-3-thiourazole	" "	1.568	(" XXXIII.
25°	Sodium 1-phenyl-3-thiourazole	Methyl "	7.20	(" X.)
50°	1-Phenyl-3-thiourazole	" "	18.88	(" XXXIV.)

thiourazole is apparently high. Further work is needed with these salts. The evidence obtained, however, seems to show that the urazole anions react with the alkyl halides.

3. If the reaction is ionic, the free 1-phenyl-3-thiourazole acid, in reacting with an alkyl halide, should give a much lower velocity constant than its salt in the same concentration, since organic acids are, as a rule, much less dissociated than their sodium salts. The velocity constant should be proportional to the percentage of ionization of the salt or acid if the action is ionic, but proportional to the concentrations of the molecular form if the reactions are molecular and *if the substitution of sodium for hydrogen makes no difference in the reaction velocity.* The experimental data show that the velocity constant for the acid is much lower than that for the salt.

The velocity constants for the action of both ethyl and methyl iodides on the urazole acid decrease in value from the beginning. This is due to the formation of hydriodic acid, which suppresses the ionization of the urazole acid, and to the change of the 1-phenylthiourazole into the disulphide. The extent of the latter reaction and the value of the constant were studied in the usual manner. Since the reaction involves the ultimate union of two thiourazole anions, the formation of the disulphide must take place according to a reaction of the second order, whether the disulphide is formed directly from anions or from the undissociated thiourazole. Although a good constant was obtained for the reaction of the second order, there is no evidence on the question as to whether the anions or the undissociated thiourazole form the disulphide. This will be investigated. A 0.05 normal solution of 1-phenyl-3-thiourazole in 50 per cent alcohol gave a value of 0.0024 for K_1 (Table XXXVI.).

The evidence harmonizes completely with the assumption that the anions react with the alkyl halides.

4. The effect of change in the concentration of the reacting agents on the value of the velocity constant is now to be considered. The equation for a second order reaction shows that if the concentration becomes n times as great, the value

of the velocity constant is also n times as great. When equimolecular quantities of the two reacting materials are used the differential equation is $\frac{dx}{dt} = K(A-x)^2$. The integral of this equation is $\frac{x}{t(A-x)} = AK$, when the value of x is zero at the beginning of the reaction.

Now, if at the beginning of the reaction the concentration of the reacting substances were n times as great, the differential equation would become $\frac{dx}{dt} = K(nA-x)^2$. The integral of this equation is $\frac{x}{t(nA-x)} = nAK$ if the value of x is zero at the beginning of the reaction. The two integrals show that in the second case, in which the value of A is taken n times as great as it is in the first case, the value of the constant, nAK, is n times as large as the value of the constant AK in the first reaction. This statement does not bring into consideration the fact that a change in the percentage of dissociation accompanies a change in concentration. An increase in concentration causes a decrease in the percentage of dissociation. Therefore, when the concentration is doubled the value of the velocity constant becomes slightly less than twice the former value on account of this decrease in the dissociation. The following table gives some data bearing on this question, and the evidence is in harmony with all the other proof that the anions of the urazoles react with the alkyl halides.

Concentration of sodium 1-phenyl-3-thiourazole.	Concentration of C_2H_5I.	AK.
0.05 N	0.05 N	0.0099
0.10 N	0.10 N	0.0158
0.20 N	0.20 N	0.0361
0.40 N	0.40 N	0.0706

See Tables I., III., IV., and V. in the experimental part.

Burke and Donnan,[1] while studying the action of alkyl iodides on silver nitrate, likewise obtained changes in the

[1] J. Chem. Soc., 85, 575, 578.

value of the velocity constants with change of concentration, as is illustrated by the following table:

Initial concentration of both C_4H_9I and $AgNO_3$.	Mean velocity constant.
0.0500 N	0.00089
0.0250 N	0.00068
0.0200 N	0.00063
0.0125 N	0.00047
Initial concentration of both C_2H_5I and $AgNO_3$.	**Mean velocity constant.**
0.025 N	0.0022
0.0125 N	0.0015

5. A change in temperature has a great effect upon the velocity constant. Between 0° and 50° the mean temperature coefficient $(K_{t^\circ+25^\circ}):K_{t^\circ}$ is 10.56. For sodium 1-phenyl-3-thiourazole and C_2H_5I the value of $K_{25^\circ}:K_{0^\circ}$ is 10.75 and of $K_{50^\circ}:K_{25^\circ}$ is 10.38. The average of these two is 10.56. Arrhenius' formula,[1] $\log K_T - \log K_o = \alpha\left(\frac{1}{T_T}-\frac{1}{T_o}\right)$, gives a fair constant for α. Between 0° and 25° α is —3352. Between 0° and 50° α is —3615. Brigg's logarithms are used. For phenylthiourazole and C_2H_5I the value of $K_{50^\circ}:K_{25^\circ}$ is 8.17. See Tables I., VI., VII., XXXIII., and XXXV. in the experimental part.

It has been proven by Jones and West[2] and by A. A. Noyes[3] and Coolidge and coworkers that a change in temperature causes only a slight change in the percentage of dissociation. The increase in the reaction velocity, then, must be due to the increased velocity of the reacting particles in the solution, to the increased tendency of the particles to react when they come in contact with each other in the solution, and, without doubt, to other causes.

6. All results point to an ionic reaction on the part of the sodium 1-phenyl-3-thiourazole and the 1-phenyl-3-thiourazole, but the alkyl halides seem to react in molecular form.

Several theories have been advanced to explain the mechanism of the reactions of alkyl halides with other substances.

[1] Z. physik. Chem., 4, 226.
[2] THIS JOURNAL, 34, 357.
[3] Z. physik. Chem., 46, 323. J. Am. Chem. Soc., 26, 134.

A. *The Theory of Lobry de Bruyn and Steger.*[1] These investigators supposed that in reactions between alkyl halides and other substances there is a very slight dissociation of the alkyl halide into alkyl and halide ions,

$$C_2H_5I \rightleftarrows \overset{+}{C_2H_5} + \overset{-}{I}$$

or

$$\frac{C_{ethyl\ ions} \times C_{iodide\ ions}}{C_{ethyl\ iodide}} = K_{ethyl\ iodide} \qquad (1),$$

and that the ions so formed then react with the ions of the other substance,

$$\overset{+}{K} + \overset{-}{OH} + \overset{+}{C_2H_5} + \overset{-}{I} \rightarrow C_2H_5OH + \overset{+}{K} + \overset{-}{I}. \qquad (1').$$

$C_{ethyl\ iodide}$ in equation (1) should be $(C_{ethyl\ iodide} - y)$, in which y is the concentration of the ethyl and iodide ions. y is so small that it can be neglected. Since the conductivity of alkyl halides in alcohol was found to be very small indeed, it was known by Bruyn and Steger that the percentage of dissociation of the alkyl halide can be only very small at most; they supposed, however, that a small amount of dissociation really exists and could account for all of the reactions. The small conductivity shown by alkyl halides in alcohol or water may be due to a slight decomposition into a halogen acid and an alkylene group, or to other reactions, as was shown by Lengfeld[2] and Hillyer,[3] working under Remsen.

It is quite true that if the reactions of the alkyl halides do depend on the primary and instantaneous ionization of the alkyl halide, only a small amount of this ionization might be necessary to give the reaction velocities actually found by experiment. We must recall that the percentage of dissociation of many of the double cyanides, potassium silver cyanide and potassium cadmium cyanide, for example, according to the expression

$$\overset{-}{Ag}(CN)_2 \rightleftarrows \overset{+}{Ag} + 2\overset{-}{CN},$$

[1] Rec. Trav. Chim., **18**, 325.
[2] This Journal, **11**, 40.
[3] *Ibid.*, **8**, 251.

is less than 10^{-15}. Yet when a solution of one of these double cyanides is treated with hydrogen sulphide, the precipitation of silver sulphide or cadmium sulphide is complete almost instantaneously. This shows, then, that the mechanism of the reaction assumed by Bruyn and Steger is not without analogy. There is one fact, however, that the other workers in the field have apparently overlooked, and that is that the reactions of alkyl halides do not follow the requirement of the mass law as applied to the explanation given by Bruyn and Steger.

If the reaction between ethyl iodide and sodium 1-phenyl-3-thiourazole were really a reaction between ethyl ions and urazole ions, according to the expression

$$\overset{+}{\mathrm{Na}} + \overline{\mathrm{Ur}} + \overset{+}{\mathrm{C_2H_5}} + \overline{\mathrm{I}} \rightarrow \overset{+}{\mathrm{Na}} + \overline{\mathrm{I}} + \mathrm{UrC_2H_5} \qquad (2),$$

and if the ions are all formed practically instantaneously in comparison with the time required for the union of the ethyl and urazole ions, the velocity of the reaction would have to be expressed by the equation

$$\frac{dx}{dt} = K_{trans} \times C_{urion} \times C_{ethyl\ ion} \qquad (3).$$

In the equation (3) we can substitute $\alpha(A-x)$ for C_{urion} in which A is the original concentration of the urazole salt, x is the change in concentration of the salt in time t, and α is the constant percentage of dissociation of the salt. From equation (1) it is clear that we can substitute for $C_{ethyl\ ion}$ in equation (3) the value $K_{ethyl\ iodide} \times \frac{C_{ethyl\ iodide}-x}{C_{iodide\ ions}}$ or $K_{ethyl\ iodide} \times \frac{(A-x)}{\alpha_1 x}$, in which $K_{ethyl\ iodide}$ is the dissociation constant of the ethyl iodide, $C_{ethyl\ iodide}$ or A is the original concentration of the ethyl iodide, x is the change in the concentration of the ethyl iodide in the time t and hence is also the concentration of the sodium iodide at the time t, α is the percentage of dissociation of the sodium iodide, and $C_{iodide\ ions}$ or $\alpha_1 x$ is the concentration of the iodide ions, which come almost entirely from the sodium iodide. Equation (3) therefore becomes equation (4),

$$\frac{dx}{dt} = K_{trans} \times K_{ethyl\ iodide} \frac{\alpha(A-x)^2}{\alpha_1 x} = \frac{K(A-x)^2}{x}, \text{ or}$$

$$K = \frac{1}{t}\left(\log n \frac{A-x}{A} + \frac{x}{A-x}\right) \qquad (4),$$

if $x=0$ when $t=0$. But the application, in equation (4), of the data in Table I. in the experimental part leads to no constant value for K, and hence this interpretation of Bruyn and Steger's hypothesis is not in harmony with the experimental facts.

If we assume a very improbable case, namely, that the ethyl iodide dissociates very slowly in comparison with the union of the ethyl ions with the urazole anions, the velocity of the formation of the ethyl urazole would depend simply upon the rapidity of the ionization of the ethyl iodide. Since the velocity of the formation of the ionization products of the ethyl iodide would depend simply upon the concentration of the ethyl iodide, it follows that the velocity of formation of the ethyl urazole would be represented by the equation (5),

$$\frac{dx}{dt} = K(A-x) \text{ or } K = \frac{1}{t} \log n \frac{A}{A-x} \qquad (5),$$

in which A is the original concentration of the ethyl iodide and sodium urazole, and x is the change in concentration of the ethyl iodide or ethyl urazole in the time t. Equation (5), however, leads to no constants. It is just as improbable, further, that the entire reaction involves (1) a measurable rapidity of the ionization of the ethyl iodide, followed by (2) slow union of the ethyl and urazole anions. The equations corresponding to this case give no constants.

At the beginning of the reaction the concentration of the iodide ions is practically zero, because the ionization of the ethyl iodide can not be appreciable. But after the formation of even a small quantity of ethylurazole and sodium iodide the concentration of the iodide ions has become enormously large in comparison with the concentration of iodide ions furnished by the ethyl iodide alone. As a result of this the equilibrium of equation (1) would be disturbed, and since the C_{iodide} in equation (1) becomes very large the value of

$\frac{C_{ethyl\ ions}}{C_{ethyl\ iodide}}$ would become correspondingly smaller, and would constantly and greatly decrease during the reaction. Since the value of $\frac{C_{urion}}{C_{urazole\ salt}}$ does not change, it is evident that the value of K_{trans} in equation (3) would have to decrease enormously during the reaction. Such, however, is not the case. The value of K_{trans} has been found by many experiments to be practically a constant. It seems certain, then, that unless some further facts concerning the mechanism of the reaction are discovered in the future the hypothesis of Bruyn and Steger that alkyl halides react with other substances through primary dissociation into alkyl and halide ions, followed by the union of the alkyl ion and the anion, cannot be correct. The subject is under investigation.

B. *The bivalent-carbon hypothesis of Nef.*[1]—Nef, after exhaustive experimental work covering a period of years, came to the conclusion that alkyl halides, sulphates, nitrates, etc., alcohols, alcoholates, etc., all react with other substances only after they dissociate, to a very slight extent, into an unsaturated carbon complex and the other constituent composing the alkyl halide, sulphate, etc. There are two methods by which such a dissociation could take place; one would lead to the formation of a bivalent-carbon complex while the other would lead to the production of an olefine derivative:

$$CH_3CH_2I \rightleftharpoons CH_3\dot{C}H\!\!\rightleftharpoons + HI,$$

$$CH_3CH_2I \rightleftharpoons CH_2{=}CH_2 + HI.$$

Whether this equilibrium is between the molecular acid and the unsaturated carbon derivative as illustrated above, or between (amphoteric) ions, as illustrated in the following expressions, cannot be decided at present:

$$CH_3CH_2I \rightleftharpoons \overset{+}{C}H_2\overset{-}{C}H\!\!\rightleftharpoons + \overset{+}{H} + \overset{-}{I},$$

$$CH_3CH_2I \rightleftharpoons \underset{\downarrow}{\overset{+}{C}H_2}\!-\!\underset{\downarrow}{\overset{-}{C}H_2} + \overset{+}{H} + \overset{-}{I}.$$

[1] Ann. Chem. (Liebig) **298**, 202–374; **309**, 126; **310**, 316–335; **318**, 1–57, 137–230; **335**, 191–333.

Nef assumed that the ethylidine reacts with some other constituent, or rearranges into an olefine:

$$CH_3CH_2I + \overset{+}{K} + \overline{O}C_2H_5 \rightleftharpoons CH_3CH \rightleftharpoons + \overset{+}{H} + \overline{I} + \overset{+}{K} +$$

$$\overline{O}C_2H_5 \longrightarrow CH_3CH \rightleftharpoons + HOC_2H_5 + \overset{+}{K} + \overline{I} \longrightarrow CH_3CH_2OC_2H_5 +$$

$$\overset{+}{K} + \overline{I}.$$

Although Nef had a large amount of experimental evidence in favor of this theory, he did not study the problem by the application of the mass law to the reactions. When this is done it is seen that there are some serious difficulties in making the facts harmonize with Nef's theory in its present form.

If Nef's latest interpretation[1] of the reactions between alkyl halides and phenylthiourazoles, for instance, were correct, and the only slow reaction were the union of the ethylidine and the urazole anion, we should have the following expressions:

$$UrH + C_2H_5I \rightleftharpoons \overline{Ur} + \overset{+}{H} + CH_3CH \rightleftharpoons + \overset{+}{H} + \overline{I} \longrightarrow$$

$$UrC_2H_5 + \overset{+}{H} + \overline{I},$$

or

$$\frac{dx}{dt} = K_{trans} \times C_{urion} \times C_{ethylidine} \qquad (1).$$

Now, at the beginning of the reaction the amount of ethylidine and of hydrogen and iodide ions is very small, at most, and could be calculated from the equation (2),

$$\frac{C_{ethylidine} \times C_H \times C_I}{C_{ethyl\ iodide}} = K_{ethyl\ iodide} \qquad (2),$$

if the value of $K_{ethyl\ iodide}$ were known. But after the formation of even a small amount of the ethylurazole and hydriodic acid, the value of the concentration of the hydrogen and iodide ions, formed by dissociation of the hydriodic acid, becomes very large indeed in comparison with the value of the concentration of these ions furnished by the ethyl iodide alone. As a result, the value of the ratio $C_{ethylidine} : C_{ethyl\ iodide}$ must decrease correspondingly, and during the reaction

[1] See Higley: Footnote, THIS JOURNAL, 37, 296.

become continuously smaller. Therefore, if Nef's theory were correct, the value of K_{trans} in equation (1) would decrease very greatly in value during the reaction. As a matter of fact it decreases only very slightly because of some secondary reactions, and, indeed, practically follows the equation

$$\frac{dx}{dt} = K_{trans} \times C_{urion} \times C_{ethyl\ iodide} \qquad (3).$$

Of course, the ratio $C_{urion} : C_{urazole}$ becomes smaller and smaller in equation (1) as the reaction proceeds, because of the suppression of the ionization of the urazole by the hydrogen ions from the hydroiodic acid formed in the reaction. Equation (3) takes this fact into consideration. The senior author of this communication is continuing the investigation of the mechanism of such alkylation reactions along physical chemical lines. It may be stated briefly here that we have not been able to harmonize Nef's theory with the experimental facts by assuming the following cases: (I.) A slow dissociation of the alkyl halide into an alkylidine and a halogen hydride, followed by a rapid or slow reversible or nonreversible union of the urazole ions or molecules with the alkylidine, or with the alkylidine and hydrogen ions, or with the alkylidine, hydrogen, and halide ions. (II.) An instantaneously reversible dissociation of the alkyl halide into an alkylidine and a halogen hydride followed by a fast or slow reversible or nonreversible union of the urazole ions or molecules with the alkylidine, alkylidine and hydrogen ions, or alkylidine, hydrogen, and halide ions. Our own work and that of Brusoff,[1] of Conrad, Hecht, and Brückner,[2] and of others, seems to show (1) that the olefine is formed by a direct loss of a halogen acid from the alkyl halide according to a monomolecular reaction, and (2) that the ester is formed from the urazole anion and the molecular alkyl halide according to a bimolecular reaction.

It seems that all the facts known at present warrant a serious doubt as to the validity of Nef's hypothesis as it is expressed at present. It may be shown later, however, by further study of the subject that certain factors not known at present must

[1] Z. physik. Chem., **34**, 129.
[2] *Ibid.*, **4**, 273, 631.

be considered, or that a modification of Nef's view may be in harmony with the truth. This subject will be discussed in great detail in a later article. Especially must it be borne in mind, however, that in such reactions as the above the *side products*, such as olefines, may be formed by independent side reactions, and not necessarily, as Nef assumes, by a change of a methylene residue into the olefine. The olefine is not necessarily an intermediate product in the alkylation reactions.

C. *The Complex-cation Hypothesis of Euler.*[1]—Euler, in a recent article, put forward the hypothesis that alkyl halides react with other substances, such as salts, because the alkyl halide first unites to a small extent with the cation and forms a complex cation, which then reacts with the anion:

$$C_2H_5I + \overset{+}{K} + \overset{-}{OH} \rightleftharpoons C_2H_5I.\overset{+}{K} + \overset{-}{OH} \longrightarrow C_2H_5OH + \overset{+}{K} + \overset{-}{I} \quad (1).$$

Euler did not subject the hypothesis to quantitative proof, and this has now been done by the writers. If equation (1) represented the true course of the reaction the following analysis would hold, whether the first or second, or both, steps in reaction (1) take place with measurable rapidity: the addition of 15 molecules of potassium iodide should cause only a slight lowering of the percentage of ionization of the potassium hydroxide present, but a very large increase in the amount of the complex cations, $C_2H_5I.\overset{+}{K}$, present at any moment, and hence should *increase* very largely the velocity constant of the reaction. Such, however, is not the case. The velocity constant of the reaction between the alkyl halide and potassium hydroxide is *lowered* by the addition of potassium iodide to just about the value calculated from the suppression of the ionization of the potassium hydroxide by the potassium iodide. The same holds true for a large number of other experiments along these lines. Furthermore, reference to Tables XLV. and XLVI. shows that the addition of ethyl iodide to an alcoholic solution of sodium phenylthiourazole hardly causes any change in the conductivity of the solution. If appreciable amounts of a complex cation or anion were formed the conductivity of the solution should be lowered

[1] Ber. d. chem. Ges., **39**, 2734.

considerably, since the ionic velocity of the complex cation or anion would be much less than that of the simple cation or anion. This quantitative evidence is not in harmony with Euler's hypothesis.

D. *The Complex-anion Hypothesis.*[1]—As far as the evidence goes it seems that alkyl halide molecules react with the anions of the salts which are alkylated. It may be that the alkyl halide forms a very unstable complex anion, $C_2H_5I.\overline{X}$, which at once yields halide ions and C_2H_5X. Such an assumption must be tested further, however, by experiment.

That such a hypothesis is in harmony with the qualitative and quantitative facts can be shown very readily. Conductivity and other quantitative evidence shows that at most only a very small amount of the complex anion can be present at any instant. The question then arises whether the decomposition of this small amount of complex anion can account for the reaction. The treatment of the subject now depends upon whether the formation of the complex anion from the alkyl halide and urazole anion is a reversible reaction or not.

Taking the first of these two possibilities, let us see what are the quantitative relations if the formation of the complex anion from the alkyl halide and the urazole anion is a reversible reaction. The equilibrium would be represented by the following equation, in which $C_{alkyl\ halide}$ and C_X would represent the concentrations of the alkyl halide and the anions at any moment if no complex anion were formed from them, y or $C_{companion}$ the concentration of the complex anion, and K_{equil} the equilibrium constant:

$$C_2H_5I + \overline{X} \rightleftharpoons C_2H_5I.\overline{X},$$

or

$$(C_{alkyl\ halide} - y)(C_X - y) = K_{equil}\, y = K_{equil} C_{companion} \quad (1).$$

If y is very small, as it is in this case, no appreciable error is involved in writing equation (1) in the form

$$C_{alkyl\ halide} \times C_X = K_{equil} C_{companion} \quad (2).$$

[1] Acree and Johnson: THIS JOURNAL, 38, 262.

If, now, the complex anion yields the ester, the rate of formation of the ester must be directly proportional, at any moment, to the concentration of the complex anion, or

$$\frac{-dC_{companion}}{dt} = K_{trans}C_{companion} \qquad (3).$$

The small amount of complex anion, $-dC_{companion}$, changed in dt, is exactly equivalent to dx, the small amount of ester formed. If the complex anion decomposes very slowly in comparison with the rapidity of its formation, it is always practically in equilibrium with the alkyl halide and the urazole ions and we can substitute for $-dC_{companion}$ and $C_{companion}$ in (3) their equivalents dx and $C_{alkyl\ halide} \times C_X$. We then get

$$\frac{dx}{dt} = K_{trans} \times C_{alkyl\ halide} \times C_X \qquad (4).$$

If we started with the concentration $C'_{alkyl\ halide}$ of alkyl halide and C_{ursalt} of urazole salt at first, and x is the amount of ester which has been formed, and α is the percentage of dissociation of the urazole salt, then

$$C_{alkyl\ halide} = (C'_{alkyl\ halide} - x) \text{ and } C_X = \alpha(C_{ursalt} - x) \quad (5).$$

We can therefore substitute for $C_{alkyl\ halide}$ and C_X in equation (4) their values in equation (5), and we then get equation (6),

$$\frac{dx}{dt} = K_{trans}\alpha(C'_{alkyl\ halide} - x)(C_{ursalt} - x),$$
$$= K(C'_{alkyl\ halide} - x)(C_{ursalt} - x) \qquad (6),$$

which is exactly the relation found experimentally.

It is clear, then, that the alkyl derivative may come from a complex anion, which has been formed in small amounts from the alkyl halide and the anion in an instantaneously reversible reaction, provided that the complex anion decomposes very slowly in comparison with the rapidity of its formation from the alkyl halide and the anion. If the equilibrium in equation (1) is established only very slowly in comparison with the rapidity of the decomposition of the complex anion into the ester and halide ions, the equations represent-

ing such a course of reactions become practically identical with those in the next case to be considered.

Another set of conditions under which the esters could be formed from a complex anion in accordance with the established quantitative data is that in which the alkyl halide and anion unite slowly in an irreversible reaction and form a complex anion which decomposes very rapidly into the ester and the halide ions. The rate of formation of the complex anion is then

$$\frac{dx}{dt} = K_{trans}\,\alpha(C_{alkyl\ halide}-x)(C_{ursalt}-x),$$
$$= K(C_{alkyl\ halide}-x)(C_{ursalt}-x) \qquad (7),$$

in which x is the concentration of the complex anion formed in the time t, $C_{alkyl\ halide}$ and C_{ursalt} the original concentrations of the alkyl halide and urazole salt, respectively, and α the percentage of dissociation of the urazole salt. But if the complex anion decomposes very rapidly, the concentration of the ester formed, y, is practically the same as x, and no measurable error is involved in substitutimg y for x in equation (7). We therefore obtain (8) for the equation expressing the velocity of formation of the ester under the above conditions. *This equation is actually found to hold experimentally.*

$$\frac{dy}{dt} = K(C_{alkyl\ halide}-y)(C_{ursalt}-y) \qquad (8).$$

These consecutive reactions can not both take place with measurable slowness; the above equations would not express the progress of the reactions. We have discussed, therefore, three sets of conditions under which a complex anion, formed by the union of an alkyl halide and an anion, could yield the alkyl derivative and a halide ion.

If the dissociation of the alkyl halides were instantaneous, we could modify the hypotheses of Bruyn and Steger and of Nef so that they would hold experimentally. But such a modification would become identical with the complex-anion hypothesis discussed above.

If the urazole ions and *both* the alkyl and halide ions, or the urazole ions and the alkylidine, hydrogen, and halide ions,

must first unite in an instantaneously reversible reaction and form a complex anion in small concentration, which then decomposes slowly according to the conditions discussed above, then the rate of formation of the ester must be expressed by the equation

$$\frac{dx}{dt} = K_{trans} \times C_{companion},$$
$$= K_{trans} \times K \times C_{ethyl\ ion} \times C_{iodide\ ion} \times C_{urion} \text{ or}$$
$$K_{trans} \times K \times C_{ethylidine} \times C_H \times C_I \times C_{urion},$$
$$= K_{trans} \times K \times C_{ethyl\ iodide} \times C_{urion},$$

which holds experimentally under all of the conditions known at present. But silver nitrate, potassium hydroxide, etc., do not react instantaneously with alkyl halides, and hence *the alkyl halides probably do not dissociate instantaneously, consequently even this modification of the hypotheses of Bruyn and Steger and of Nef does not seem to hold experimentally.*

That the alkyl halide molecules may react with the anions, however, is made probable from the fact, shown by Jones[1] and his coworkers, that neutral water forms hydrates with anions, and from the observations of Acree and Johnson[2] that acetone molecules react with hydroxylammonium ions, neutral water molecules with complex ester cations, neutral alcohol molecules with acetic acid cations, $CH_3COOH.\overset{+}{H}$, and water molecules with cane sugar cations, $(C_6H_{11}O_5)_2\overset{+}{O}H$. Acree and Nirdlinger[3] showed also that acetamide cations, $CH_3C\overset{+}{O}NH_3$, are hydrolyzed in water. All of these reactions are essentially alike.

If the alkyl halide forms an unstable compound with the anion it may be because of the unsaturated condition of the halogen of the alkyl halide or of the anion, or of both, and exactly the same reason may apply to the formation of the alkyl halide addition products of amines, dialkyl sulphides, R_2S, and other substances. That alkyl iodides react more

[1] See H. C. Jones and coworkers "Hydrates in Aqueous Solution," Publication No. 60, Carnegie Institution of Washington.

[2] THIS JOURNAL, **37**, 410; **38**, 308.

[3] *Ibid.*, **38**, 489.

readily than alkyl bromides, and these more readily than alkyl chlorides, may be due to the greater tendency of the iodine to react with or absorb the anions of other groups. The fact that primary, secondary, and tertiary alkyl halides decrease in activity in the order given may be connected with the so-called space interference, as well as with the reasons discussed above. The field is a ripe one for investigation and the work outlined above will be continued.

7. Thus far all the arguments used to prove that the reaction between sodium 1-phenyl-3-thiourazole and alkyl halides is an ionic one on the part of the urazoles have been based on our knowledge of the behavior of an electrolyte in water solution. The reactions took place, however, in a 50 per cent ethyl alcohol solution, and the reaction constant is not the same as in pure water. That it is nearly the same, however, is proven by a study of the alkylation of sodium 1-phenyl-3-thiourazole by sodium chloracetate.

0.2 N sodium thiourazole + 0.2 N ClH_2COONa in water at 50°. $K_1 = 0.189$.

0.2 N sodium thiourazole + 0.2 N ClH_2COONa in 50 per cent alcohol at 50°. $K_1 = 0.15$.

See Tables XXXVII. and XXXVIII. in the experimental part.

Euler,[1] in his work on the action of chloracetic acid on silver nitrate, obtained results which were still closer.

Concentration in reaction mixture.		1000 K (80°).	
Chloracetic acid.	Silver nitrate.	Water.	45 per cent alcohol.
0.25	0.25	1.776	1.766
0.125	0.25	1.82	....
0.25	0.125	....	1.77
0.20	0.20	1.80	1.80

It is clear, then, that the fact that 50 per cent alcohol was the solvent used does not detract in the least from the validity of the evidence that the reaction is one between the urazole anions and the molecular alkyl halide.

8. When the alkyl group is the same, the velocity constant varies with the change of the halide in this order: for the

[1] *Loc. cit.*

iodide it is greater than for the bromide, and greater for the bromide, in turn, than for the chloride. This agrees with the results of other investigators whose work will be given later. The following table is a summary of the velocity constants (at 25°) of the reactions described:

Alkyl (normal).	Halide.			Ratio.		
	Iodide.	Bromide.	Chloride.	Iodine.	Bromine.	Chlorine.
CH_3	7.20	.....	.....	...	....	.....
C_2H_5	0.316	0.117	.....	I	0.37	.....
C_3H_7	0.201	0.076	0.00130	I	0.38	0.093
C_4H_9	0.214	0.074	0.00364	I	0.35	0.017

Slator[1] got similar results in the reaction of sodium thiosulphate on the monohalide acetates.

Values of velocity constants at 25°.

Ethyl iodoacetate.	Ethyl bromacetate.	Ethyl chloracetate.
7.00	6.40	0.06

Ratio.	Iodine.	Bromine.	Chlorine.
	I.000	0.914	0.0086

Slator[2] obtained the following ratios from the action of alkyl halides on sodium thiosulphate:

Alkyl.	Iodine.	Bromine.	Chlorine.
CH_3	I	I	0.0025
C_2H_5	I	0.62	(very small)

Menschutkin[3] got the following ratio from the action of allyl halides on organic amines:

Iodine.	Bromine.	Chlorine.
I	0.166	0.00166

It is evident, then, that our results are in harmony with those of other investigators and show beyond question that the alkyl iodides have the highest reactivity. Closely following, however, in their reactivity, come the alkyl bromides, while the alkyl chlorides lag far behind.

9. The following table shows how the values of the velocity constants, in the reactions of alkyl halides with sodium thio-

[1] J. Chem. Soc., **87**, 481.
[2] *Ibid.*, **88**, 1287.
[3] Z. physik. Chem., **86**, 52.

urazole at 25°, vary with the character of the alkyl group. Read down.

Table A.

	Halide.		
Alkyl.	Iodide.	Bromide.	Chloride.
Methyl	7.20	....	....
Ethyl	3.16	0.1170	....
n-Propyl	0.20	0.0764	0.00130
n-Butyl	0.214	0.0742	0.003640
n-Hexyl	0.0094	.....	....
n-Octyl	0.0159	.....	....
n-Cetyl	0.00132	.....	....
Isoamyl	0.0464	0.03560	0.001070
Isopropyl	0.0222	0.00626	0.000800
Isobutyl	0.0085	0.00640	0.000290
Tert. butyl	0.00088	0.00110	0.00055

The value of the constant varies greatly with the constitution in an isomeric series. In general, the secondary alkyl halide is less reactive than the primary, and the tertiary less reactive than the secondary. It will be noticed in Table B that the reactivity of the tertiary butyl iodide, bromide, and chloride does not decrease in the order given, as is generally found with the alkyl halides. In general, one must expect the relative reaction velocities of the different alkyl halides to vary with the nature of the substances with which the alkyl halides react.

Table B.

Alkyl.	Iodide.	Bromide.	Chloride.
n-Butyl	0.21400	0.07400	0.00364
Isobutyl	0.00850	0.00640	0.00029
Tert. butyl	0.00088	0.00110	0.00055

In the normal series the constant decreases with increase in the weight of the alkyl group, but the decrease is not nearly so large as that caused by the complexity of the group (side chains). Compare Tables A and B, above. It is evident that the so-called space interference may play the same rôle in these reactions that other investigators have noticed in entirely different reactions. In order to show the general relations, a resumé of some of the more important researches

dealing with, or showing, the so-called space interference is made in this section.

Wislicenus[1] studied the action of alkyl iodides on ethyl sodium acetoacetate in ethyl alcoholic solution and obtained the following results:

Table C.

Iodide.	Relative velocity.
Methyl	196
Ethyl	21
n-Propyl	5
Isopropyl	1–9
Tert. butyl	(very small)
Allyl	784+

Menschutkin[2] obtained the following results with triethylamine in acetone solution at 100°:

Table D.

Iodide.	Relative velocity.	Iodide.	Relative velocity.
Methyl	1140.00	*n*-Butyl	1.38
Ethyl	10.10	*n*-Heptyl	1.08
n-Propyl	1.93	*n*-Octyl	1.00

Menschutkin also obtained the following results in his work on triethylamine and alkyl halides in acetone solutions:

Table E.

Alkyl.	Iodide.	Bromide.	Alkyl.	Iodide.
Ethyl	0.0608	0.00958	*n*-Butyl	0.00832
n-Propyl	0.0116	0.00165	Isobutyl	0.00191
n-Butyl	0.0083	0.00123	*n*-Propyl	0.0116
n-Heptyl	0.0065	0.00119	Isopropyl	0.00121
n-Octyl	0.0060	0.00110		

Hecht, Conrad, and Brückner[3] worked with alkyl iodides and sodium ethoxide in ethyl alcoholic solution at 30°, and obtained the following results:

Table F.

Iodide.	Relative velocity.	Iodide.	Relative velocity.
Methyl	61.72	Isopropyl	0.92
Ethyl	4.87	*n*-Heptyl	1.04
n-Propyl	1.71	*n*-Octyl	1.00

[1] Ann. Chem. (Liebig), **212**, 239.
[2] Z. physik. Chem., **5**, 589.
[3] *Ibid.*, **4**, 273, 631.

Burke and Donnan[1] worked with alkyl iodides and silver nitrate and found the relative reaction velocities to decrease in the following order: isopropyl, ethyl, *n*-propyl, methyl, *n*-butyl, isoamyl, isobutyl.

Slator[2] studided the action of sodium thiosulphate on the esters of monohalogen substitution products of acetic acid.

Table G.

Halide substitution product.	Relative velocity.
Ethyl iodoacetate	118.64
Ethyl bromacetate	108.47
Methyl bromacetate	99.15
Ethyl chloracetate	1.017
Methyl chloracetate	1.00

Menschutkin,[3] in his work on the influence of chemical constitution on the speed of esterification, has obtained results which, in general, are analogous:

Table H.

Primary alcohols.	Initial velocity.	Relative velocity.	Limit of esterification.
Methyl	55.60	.....	67.52
Ethyl	46.95	70.52	66.57
Propyl	46.92	70.18	66.85
Butyl	46.85	69.61	67.30
Octyl	46.59	64.40	72.34
Isobutyl	42.36	66.66	67.38

Acids with primary radicals.

Table I.

Acid.	Initial velocity.	Limit of esterification.
Formic	61.69	64.23 at 100°
Acetic	44.36	67.36 at 155°
Propionic	41.18	68.70 at 155°
n-Butyric	33.25	69.52 at 155°
n-Caproic	33.08	69.81 at 155°
n-Caprylic	30.86	70.87 at 155°

From the above work the following conclusions were drawn by Menschutkin:

[1] J. Chem. Soc., **85**, 555.

[2] *Ibid.*, **87**, 481.

[3] Ann. Chem. (Liebig), **195**, 334; **197**, 193. Ann. Chim. Phys., [5], **23**, 14. Ber. d. chem. Ges., **10**, 1728; **11**, 679, 1507, 2117, 2148. Compt. rend., **105**, 1016.

(1) "The primary alcohols possess the highest limit of esterification and the greatest initial velocity. In the series given in Table H the velocity and limit vary regularly with the molecular weight."

(2) "The initial velocity and limit of the secondary alcohols are less than the primary alcohols; analogous differences in composition correspond with analogous differences of esterification."

(3) "The velocity and limit of the tertiary alcohols are very small, and they decompose during esterification."

(4) "The primary monobasic acids possess the smallest limit of esterification and the highest initial velocity. In the series given in Table I the limit and velocity vary regularly with the molecular weight of the acid."

(5) "The secondary acids show smaller initial velocities but higher limits of esterification than the primary acids; the effect of variation of composition is not marked."

(6) "The tertiary monobasic acids, whether of the fatty or aromatic series, are characterized by the smallest velocity, but by the highest limit of esterification."

Esterification of Aromatic Acids.

This work was done by Victor Meyer[1] with Fischer's method for esterification. The work, in general, gave valuable results as to the influence of chemical constitution on the speed of reaction, and they agree with the others given above. The conclusions which bear on our work on the urazoles was summed up as follows:

The speed of esterification is diversely influenced by substituting groups or elements of different relative mass. Symmetrical trisubstituted carboxylic acids are not esterified unless the carboxyl group is joined by one or more carbon atoms to the benzene nucleus. Symmetrical trichlor-, tribrom-, and trinitro-, and 2,6-dibrombenzoic acid are not esterified; thymolic, 2,6-hydroxyphenylbenzoic, and mesitylenecarboxylic acids are esterified.

Heating causes an increased action in some cases. Those

[1] Meyer and Sudborough: Ber. d. chem. Ges., **27**, 510, 1580, 3146. Meyer: *Ibid.*, **28**, 182, 1254, 2773, 3197; **29**, 830, 839, 1397. Z. physik. Chem., **24**, 219.

radicals which prevent a reaction at high temperatures have a much greater relative mass than those which hinder action at lower temperature.

The groups OH, CH_3, and F in the two ortho positions retard the formation of ethereal salts, while Cl, Br, I, and NO_2 prevent it altogether.

When working with isomeric compounds, those containing substituting groups in the meta position are perhaps most readily acted upon, the para compounds nearly to the same extent as the meta, and the ortho compounds least. Results obtained by Kellas[1] agree with this last statement, as shown by the following table:

Table J.

	Relative velocity.					
Position.	Cl.	Br.	I.	NO_2.	CH_3.	OH.
Ortho	35.7	7.0	9.3	4.2	28.4	15.3
Meta	55.2	18.4	28.3	22.3	63.8	55.9
Para	53.1	17.2	26.8	22.3	71.0	51.3

The order of the reaction velocity for ortho acids is as follows: Benzoic, chlorbenzoic, toluic, brombenzoic, iodobenzoic, nitrobenzoic; but toluic comes before chlorbenzoic for the meta and para acids, and nitro before iodo for meta acids. Therefore the effect of the molecular weight is only comparable for analogous compounds. In hydrolysis the velocity is least for ortho acids.

Brussoff[2] worked with 2-normal potassium hydroxide and alkyl iodides in 96 per cent alcohol at 78°. The following table shows the relative maximum velocity of the evolution of the corresponding olefine.

Table K.

Iodide.	Relative maximum velocity.
Ethyl	1.66
Propyl	2.24
Isopropyl	2.86
n-Butyl	1.00
Isobutyl	2.84
Secondary butyl	5.06
Tertiary butyl	8.00

[1] Z. physik. Chem., **34**, 221.
[2] *Ibid.*, **34**, 129.

(1) "This shows that the mechanism of the reaction is different from that of the preceding work. The work shows that the velocity of the formation of the olefine is greatest from the iodides, from the bromides it is less, and it is smallest from the chlorides."

(2) "A change of solution from ethyl to methyl alcohol, or a change of alkali from potassium hydroxide to sodium hydroxide, has little effect on the velocity of formation of the olefine."

(3) "The amount of olefine formed, as well as the velocity of its formation, depends but little upon the primary, secondary, or tertiary constitution of the carbon chain, but primarily upon the number of side chains and their proximity to the side chain containing the halogen atom."

Our work, then, on the action of various alkyl halides on the salts of urazoles shows that the same stereochemical relations are involved in these alkylation reactions as were discovered in the various reactions discussed above.

10. *Results Similar to those Described in the Urazole Work.*

(1) *The speed of reaction of sodium 1-phenyl-3-thiourazole on sodium monochloracetate* was studied, both in water solution and in 50 per cent alcohol solution. All solutions were 0.2 N and the temperature was 50°. The value of K_1 in water solution was 0.189, while in 50 per cent alcohol solution K_1 was 0.150. See Tables XXXVII. and XXXVIII. in the experimental part. The sodium chloracetate was made by titrating a boiling solution of sodium bicarbonate, 20 cc. N solution, with chloracetic acid in the presence of phenolphthalein. The solution was then made up to 100 cc.

(2) *The action of sodium thioacetate on ethyl iodide* was investigated. The solutions used were 0.2 N, and the temperature was 25°. The sodium thioacetate was made by titrating 20 cc. of N sodium hydroxide with a water solution of thioacetic acid until the red color of phenolphthalein disappeared. The solution was then made up to 100 cc. The value of K_1 was found to be 0.40. See Table XXXIX. in the experimental part.

(3) *Action of N potassium hydroxide upon N ethyl iodide.*—It was suspected that when the alkyl halides react with alkali hydroxides, the reaction is really between the molecular alkyl halide and the hydroxyl ions. The following equation was found to express approximately the course of the reaction:

$$\frac{dx}{dt} = K_{trans}\,\alpha(A - x)(A - x) = K(A - x)^2 \qquad (1).$$

K_{trans} is the velocity constant, α the percentage of dissociation of the potassium hydroxide, A the original concentration of both the alkyl halide and the potassium hydroxide, and x the change in concentration of these two substances in the time t. If equation (1) expresses the reaction it is evident that the addition of potassium iodide should lower the value of α, and hence of K_1, *unless the potassium iodide has a large positive catalyzing effect.* In our work, since the data are lacking, α was assumed to be the same in 50 per cent alcohol as in water, and the formation of potassium alcoholate was left out of account. Since the potassium hydroxide and potassium alcoholate both react with the alkyl halide in independent side reaction, and since α is used only for comparison, the error involved in the assumptions is not large, but can well account for the difference between the theoretical and observed values of K_1.

$A\,K$ in Table XL. was found to be 0.011, while in the presence of 5 molecular portions of potassium iodide the value of $A\,K$ was lowered to 0.00614 instead of the calculated value 0.0082. The values of μ_v in 0.5 N and 3 N solutions were assumed to be 184 and 137.

The N potassium hydroxide solution was made by neutralizing barium hydroxide with potassium sulphate. The resulting solution was evaporated to a small volume in platinum dishes. The carbonate formed during evaporation was precipitated with barium hydroxide and the solution was then made normal by titrating it against N sulphuric acid and diluting it properly. K_1 was found to be 0.022. When the action was suppressed with 5 molecular portions of potas-

sium iodide K_1 was lowered to 0.0123. See Tables XL. and XLI. in the experimental part.

(4) *Action of N potassium hydroxide upon N methyl iodide.* K_1 was found to be 0.178. When suppressed as before, K_1 was 0.085. The value of K_1 fell with considerable regularity, due to hydrolysis of the methyl iodide in 50 per cent alcoholic solution. To study the velocity of this hydrolysis a 0.5 N solution in 50 per cent alcohol, which has the same concentration as the reaction mixture above, was made and the velocity of the reaction was then determined as usual. The value of the concentration of the water hardly changes, and the methyl iodide is the only substance appreciably diminishing in concentration. The hydrolysis of the methyl iodide should follow approximately the equation for a reaction of the first order during the first part of the reaction, before the reverse reaction is appreciable. K was found to be 0.00023. See Tables XLII., XLIII., and XLIV., in the experimental part.

The reactions between potassium hydroxide and alkyl halides furnish excellent proof that, just as with the urazoles, the hydroxyl anion reacts with the molecular alkyl halide.

$$\overline{OH} + C_2H_5I \rightleftarrows C_2H_5I.\overline{OH} \rightarrow \overline{I} + C_2H_5OH.$$

EXPERIMENTAL.

The 1-phenyl-3-thiourazole was prepared according to the method described by Acree.[1] The ethyl 1-phenylthiosemicarbazide-1-carboxylate was purified by extraction in a Soxhlet apparatus with alcohol, and crystallization. It melted at 221°. By this method a pure 1-phenyl-3-thiourazole, m. p. 192°–193°, was obtained.

The sodium 1-phenyl-3-thiourazole was made by weighing out a quantity of the phenyl-3-thiourazole and titrating this with the theoretical amount of purified and dried sodium bicarbonate in solution. The solution was evaporated to dryness, heated to constant weight, and placed in a desiccator. To make solutions of the required normality from this salt, the theoretical weight was dissolved in water and diluted to

[1] Ber. d. chem. Ges., **36**, 3151.

the required volume. The alkyl halides were made by Kahlbaum and were redistilled before use.

Unless otherwise stated, all alkyl halide solutions were made in absolute alcohol as follows: A measuring flask was nearly filled with absolute alcohol and weighed. Then a slight excess of the alkyl halide (the volume was calculated from its specific gravity) was measured into the flask, which was then weighed a second time. The flask was then kept in the thermostat until a temperature of 25° was reached, and it was then filled to the mark. The amount of absolute alcohol necessary to dilute the alkyl halide solution to the proper strength was then added. These solutions of sodium salt and alkyl halide were kept in a bath at 25°. Ten cc. portions of each were then measured into test tubes by means of carefully graduated pipettes; the concentrations at the top of each table in the experimental part refer to the separate solutions before they were mixed. The urazole solution was measured in first, because the evaporation from the water solution was slight. Then the solution of alkyl halide was added, the point of the pipette being kept below the liquid in the test tube to prevent evaporation. The test tubes were then tightly corked, and, after various time intervals, were quickly poured into 200 cc. of water, containing 4 cc. of starch solution. This resulting solution was then quickly titrated with a standard iodine solution. The alkylation reaction was, of course, nearly stopped by the large dilution with water.

The bath was the one used in the conductivity measurements. The water was kept well stirred with a water motor and propeller and the temperature was carefully regulated.

The error in titration was slight, as it was found that sodium 1-phenyl-3-thiourazole titrates with iodine as sharply as does a thiosulphate.

The error due to the hydrolysis or decomposition of the alkyl halide in the water solution was noticeable. This tended to reduce the speed of the alkylation and so lowered the constant. See Table XLIV., and also the note to Table XL.

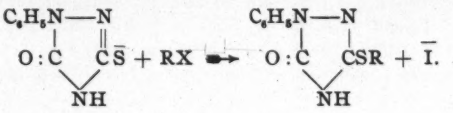
A third error was introduced by the formation of 1-phenyl-3-thiourazole through the hydrolysis of the sodium 1-phenyl-

3-thiourazole by water. The phenyl-3-thiourazole is more slowly alkylated than the sodium salt. This tends to lower the constant.

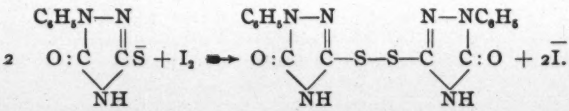
A fourth error could arise from the reaction of the sodium hydroxide, formed by the hydrolysis of the sodium phenyl-3-thiourazole, with the alkyl halide. By this reaction the concentration of the alkyl halide, and consequently the value of the constant, is lowered.

The error due to the volatilization of the alkyl halide was carefully guarded against, but must be appreciable. Rubber stoppers were used in the test tubes when the experiments were performed at 50°.

The reaction of the alkyl halides on the sodium thiourazole proceeds as follows:



The action of iodine on the sodium 1-phenyl-3-thiourazole is the following:



In obtaining the data for the following tables all of the values are expressed in terms of cc. of standard iodine solution; these are directly proportional to cc. of standard solution, and therefore weights, of sodium 1-phenyl-3-thiourazole (or acid). A is the original amount of sodium 1-phenylthiourazole taken for each titration, x is the amount changed in time t, and $A-x$ is the unchanged urazole salt (or acid). We assumed that the alkyl halides react only with the ions of the sodium 1-phenyl-3-thiourazole (or acid), and are not appreciably hydrolyzed or decomposed. Then A, x, and $A-x$ can

also represent the corresponding values of the alkyl halides. t is expressed in minutes.

The values for the amounts of the phenylalkylthiourazole formed could also be used. A could be calculated theoretically from the original concentration of sodium 1-phenyl-3-thiourazole, or the alkyl derivative formed could be separated and weighed after each experiment is complete. Both of these methods have been used in previous work by Acree,[1] Brunel, and Johnson. A and x would then represent the amount of phenylalkylthiourazole formed after time t.

The values of A_1K_1 and K_1 given with each table are calculated on the basis that A is some multiple of 10 cc., and K_1 is the value of the velocity constant when the concentration is 1 gram molecule per liter. K_1 should be, and is, nearly independent of the concentration because the percentage of ionization of the salt changes very little with the change in concentration employed in these experiments. The solvent was 50 per cent alcohol unless otherwise stated. The concentrations given at the head of each table are those of the individual solutions before they were mixed.

Table I.

25°. 0.1 N sodium 1-phenyl-3-thiourazole +0.1 N C_2H_5I.

t.	A.	$A-x$.	x.	AK.
35	10.95	6.81	4.14	0.0174
60	10.95	5.42	5.53	0.0170
120	10.95	3.58	7.37	0.0172
240	10.95	2.20	8.75	0.0166
			Average,	0.0173

$A_1K_1 = 0.0158$ and $K_1 = 0.316$

The effect of various organic and inorganic substances on the velocity constant of the reaction between 0.1 N sodium 1-phenyl-3-thiourazole and 0.1 N C_2H_5I was studied.

[1] This Journal, 37, 71.

Table II.

t.	*A.*	*A—x.*	*x.*	*AK.*			
120	10.95	3.80	7.15	0.0156	3 mols	NaCl	(0.1754 grams)
120[1]	10.95	4.11	6.84	0.0138	3 "	$NaNO_3$	(0.2551 ")
120[2]	10.86	4.50	6.37	0.0118	3 "	KNO_3	(0.3035 ")
120	10.86	4.80	7.06	0.0154	3 "	Na_2SO_4	(0.4262 ")
120	10.86	3.70	7.16	0.0161	3 "	$NaI.2H_2O$	(0.5516 ")
120	10.86	4.00	6.86	0.0150	10 "	NaI	(1.4986 ")
120	10.86	4.26	6.62	0.0130	15 "	NaI	(2.2479 ")
120	10.86	4.96	6.90	0.0145	15 "	KBr	(1.7866 ")
120	10.86	3.98	6.88	0.0144	15 "	NaBr	(1.5445 ")
120	10.86	4.27	6.58	0.0128	15 "	$BaCl_2.2H_2O$	(3.3947 ")
120	10.86	3.36	7.50	0.0186	20 "	urea	(1.2012 ")
120	10.86	3.54	7.32	0.01715	10 "	cane sugar	(3.4218 ")
+120	10.86	3.54	7.32	0.01715	10 "	" "	(3.4218 ")
120	10.86	3.38	7.48	0.0184	15 "	glucose	(2.7014 ")
120	10.86	3.35	7.51	0.0186	10 "	mannite	(1.8211 ")

[1] The very great suppression caused by sodium nitrate and potassium nitrate may be explained by assuming that these salts react with ethyl iodide and form ethyl nitrate. This, in turn, may be hydrolyzed and form nitric acid or may react with sodium 1-phenyl-3-thiourazole and give 1-phenyl-3-ethylthiourazole. This nitric acid would react with the sodium 1-phenyl-3-thiourazole and form phenyl-3-thiourazole, which would be alkylated much more slowly than the sodium 1-phenyl-3-thiourazole. All of these changes would tend to aid the suppression of the value of the constant.

[2] This experiment was repeated and gave identical results.

39
08

Table III.

25°. 0.05 N Sodium 1-phenyl-3-thiourazole +0.05 N C_2H_5I

t.	*A.*	*A*—*x.*	*x.*	*AK.*
30	4.72	3.65	1.07	0.00977
60	4.72	3.02	1.70	0.00938
180	4.72	1.795	2.925	0.00905
310	4.72	1.09	3.63	0.00922

Average, 0.00935

A_1K_1 = 0.00991 and K_1 = 0.396

Table IV.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole +0.2 N C_2H_5I.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
15	18.88	12.29	6.59	0.0357
32	18.88	8.90	9.98	0.0350
60	18.88	6.00	12.88	0.0357
120	18.88	3.43	15.45	0.0375

Average, 0.0359

A_1K_1 = 0.0361 and K_1 = 0.361

Table V.

25°. 0.4 N Sodium 1-phenyl-3-thiourazole +0.4 N C_2H_5I.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
15	37.76	19.00	18.76	0.0658
30	37.76	12.80	24.96	0.0650
45	37.76	9.47	28.29	0.0663
60	37.76	7.20	30.475	0.0697

Average, 0.0667

A_1K_1 = 0.0706 and K_1 = 0.352

The average value for K_1 in Tables I., III., IV., and V. is 0.36.

Table VI.

50°. 0.1 N Sodium 1-phenyl-3-thiourazole +0.1 N C_2H_5I.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
10	9.44	3.80	5.64	0.148
20	9.44	2.26	7.18	0.159
40	9.44	1.30	8.14	0.156
81	9.44	0.70	8.74	0.154
190	9.44	0.30	9.14	0.160

Average, 0.155

A_1K_1 = 0.164 and K_1 = 3.28

Table VII.

0°. 0.1 N Sodium 1-phenyl-3-thiourazole + 0.1 N C_2H_5I.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
30	10.86	10.03	0.83	(0.00275)
60	10.86	9.70	1.16	0.00191
120	10.86	9.06	1.80	0.00168
563	10.86	6.09	4.77	0.00139
1080	10.86	4.28	6.58	0.00142

Average, 0.00160

A_1K_1 = 0.00147 and K_1 = 0.029

Table VIII.

25°. 0.2 N Barium 1-phenyl-3-thiourazole + 0.2 N C_2H_5I.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
15	19.80	13.55	6.25	0.0307
30	19.80	10.00	9.80	0.0326
60	19.80	6.86	12.94	0.0316
120	19.80	4.10	15.70	0.0319

Average, 0.0317

A_1K_1 = 0.032 and K_1 = 0.32

15 mols. $BaCl_2.2H_2O$ (6.4070 grams) added.

128	19.80	7.25	12.55	0.0135

After standing two days in the cold and one day at 75° only half a drop of iodine was required for the titration, so the reaction was complete.

Table IX.

25°. 0.2 N Magnesium 1-phenyl-3-thiourazole + 0.2 N C_2H_5I.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
15	16.908	11.15	5.758	0.0344
30	16.908	8.14	8.768	0.0359
60	16.908	5.20	11.708	0.0375
120	16.908	2.70	14.208	(0.0438)

Average, 0.0359

A_1K_1 = 0.0425 and K_1 = 0.425

Table X.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole +0.1 N CH_3I.

t.	*A.*	*A—x.*	*x.*	*AK.*
5	10.86	3.50	7.36	0.420
10	10.86	2.30	8.56	0.371
20	10.86	1.33	9.53	0.358
30	10.86	0.78	10.08	0.416
60	10.86	0.56	10.30	(0.306)
120	10.86	0.67	10.19	(0.126)

Average, 0.391

$A_1K_1 = 0.360$ and $K_1 = 7.20$

5 mols. NaI (0.7493 gram) added.

120	10.86	2.81	8.05	0.0238

Table XI.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole + 0.1 N *n*-propyl iodide.

t.	*A.*	*A—x.*	*x.*	*AK.*
30	10.86	8.09	2.77	0.0114
60	10.86	6.60	4.26	0.0107
120	10.86	4.70	6.10	0.0107
240	10.86	3.00	7.86	0.0109

Average, 0.0109

$A_1K_1 = 0.010$ and $K_1 = 0.20$

5 mols. NaI (0.7493 gram) added.

120	10.86	5.19	5.67	0.0091

Table XII.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole + 0.1 N isopropyl iodide.

t.	*A.*	*A—x.*	*x.*	*AK.*
30	10.86	10.24	0.62	(0.00203)
60	10.86	10.07	0.79	0.00137
120	10.86	9.54	1.32	0.00115
240	10.86	8.60	2.26	0.00109

Average, 0.0012

$A_1K_1 = 0.0011$ and $K_1 = 0.022$

5 mols. NaI (0.7493 gram) added.

120	10.86	9.70	1.16	0.000997

Table XIII.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole + 0.1 N *n*-butyl iodide.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
30	10.86	7.95	2.91	0.0122
60	10.86	6.50	4.36	0.0112
120	10.86	4.565	6.295	0.0115
240	10.86	2.90	7.96	0.0114
				Average, 0.0116

$A_1K_1 = 0.0107$ and $K_1 = 0.214$

Table XIV.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isobutyl iodide.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
240	19.00	15.30	3.70	0.001004
480	19.00	13.57	5.43	0.000833
1320	19.00	9.78	9.22	0.000714
				Average, 0.00080

$A_1K_1 = 0.00085$ and $K_1 = 0.0085$

Table XV.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N ter. butyl iodide.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
30	21.76	21.14	0.62	(0.000977)
240	19.00	18.40	0.60	0.000136
480	19.00	18.30	0.70	0.0000795
1320	19.00	18.11	0.89	0.0000372
				Average, 0.0000842

$A_1K_1 = 0.0000886$ and $K_1 = 0.00088$

Table XVI.

For this table and the three following this formula was used: $(A-B)K = \frac{1}{t} \log \frac{B(A-x)}{A(B-x)}$.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.066 N *n*-hexyl iodide.

t.	*A.*	*A*—*x.*	*x.*	*B*—*x.*	*B.*	(*A*—*B*)*K.*
30	19.00	18.49	0.51	5.82	6.33	(0.000822)
240	19.00	16.59	2.41	3.92	6.33	0.000621
420	19.00	15.60	3.40	2.93	6.33	0.000592
1320	19.00	13.43	5.57	0.76	6.33	0.000582

Average, 0.000601
$(A_1-B_1)K_1$ = 0.00063
and K_1 = 0.0095

Table XVII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.066 N *n*-octyl iodide.

t.	*A.*	*A*—*x.*	*x.*	*B*—*x.*	*B.*	(*A*—*B*)*K.*
30	19.00	18.08	0.92	5.41	6.33	(0.00135)
240	19.00	15.70	3.30	3.03	6.33	0.000987
420	19.00	14.54	4.46	1.87	6.33	0.000983
1320	19.00	12.90	6.10	0.23	6.33	(0.000201)

Average, 0.000985
$(A_1-B_1)\ K_1$ = 0.00103
and K_1 = 0.16

Table XVIII.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole + 0.033 N *n*-cetyl iodide.

t.	*A.*	*A*—*x.*	*x.*	*B*—*x.*	*B.*	(*A*—*B*)*K.*
120	9.50	9.37	0.13	3.036	3.166	0.0000193
240	9.50	9.27	0.23	2.936	3.166	0.0000508
480	9.50	9.06	0.44	2.726	3.166	0.0000718
1500	9.50	9.02	0.48	2.680	3.166	0.0000259

Average, 0.0000419
$(A_1-B_1)\ K_1$ = 0.0000441
and K_1 = 0.00132

Table XIX.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole + 0.05 N iso-amyl iodide.

t.	*A.*	*A*—*x.*	*x.*	*B*—*x.*	*B.*	(*A*—*B*)*K.*
120	9.50	7.32	2.18	2.57	4.75	0.00128
240	9.50	6.44	3.06	1.69	4.75	0.00117
480	9.50	5.67	3.83	0.92	4.75	0.00102
1500	9.50	4.84	4.66	0.09	4.75	0.000953

Average, 0.0011

$(A_1—B_1)\ K_1 = 0.00116$

and $K_1 = 0.046$

Table XX.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N ethyl bromide.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
30	19.22	14.28	4.94	0.01153
60	19.22	11.60	7.62	0.01095
120	19.22	8.10	11.12	0.01144
240	19.22	5.24	13.98	0.01111

Average, 0.01126

$A_1K_1 = 0.0117$ and $K_1 = 0.117$

15 mols. NaBr (1.5445 grams) added.

120	19.22	9.30	9.92	0.00888

Table XXI.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N *n*-propyl bromide.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
30	19.22	15.52	3.70	0.00761
60	19.22	13.48	5.74	0.00709
120	19.22	10.30	8.92	0.00721
240	19.22	6.89	12.33	0.00745

Average, 0.00734

$A_1K_1 = 0.00764$ and $K_1 = 0.076$

Table XXII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isopropyl bromide.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
30	19.22	18.68	0.54	(0.000963)
120	19.22	17.84	1.38	0.000644
240	19.22	16.82	2.40	0.000594
420	19.22	15.52	3 70	0.000568
			Average,	0.000602

A_1K_1 = 0.000626 and K_1 = 0.0063

Table XXIII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N *n*-butyl bromide.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
60	19.10	13.22	5.88	0.00741
120	19.10	10.07	9.03	0.00747
'240	19.10	7.10	12.00	0.00704
360	19.10	5.50	13.60	0.00687
480	19.10	4.53	14.57	0.00670
			Average,	0.0071

A_1K_1 = 0.00743 and K_1 = 0.074

Table XXIV.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isobutyl bromide.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
120	19.10	17.50	1.60	0.000761
240	19.10	16.40	2.70	0.000687
480	19.10	15.31	3.79	0.000516
660	19.10	14.52	4.59	0.000480
			Average,	0.000611

A_1K_1 = 0.000640 and K_1 = 0.0064

Table XXV.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N ter. butyl bromide.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
120	19.10	18.80	0.30	0.000132
240	19.10	18.70	0.80	0.000182
480	19.10	18.63	0.47	0.0000525
660	19.10	18.45	0.65	0.0000534

Average, 0.000105

A_1K_1 = 0.000110 and K_1 = 0.0011

Table XXVI.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isoamyl bromide.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
30	19.22	17.43	1.79	0.00342
70	19.22	15.46	3.76	0.00347
120	19.22	13.74	5.48	0.00333
240	19.22	10.54	8.68	0.00343

Average, 0.00342

A_1K_1 = 0.00356 and K_1 = 0.0356

Table XXVII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N *n*-propyl chloride.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
60	18.88	18.58	0.30	(0.000269)
240	18.88	18.30	0.58	0.000132
660	18.88	17.45	1.43	0.000128
1440	18.88	16.30	2.58	0.000110

Average, 0.00012

A_1K_1 = 0.00013 and K_1 = 0.0013

15 mols. NaCl (0.8769 gram) added.

660	18.88	17.75	1.13	0.0000965

Table XXVIII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isopropyl chloride.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
120	18.88	18.58	0.30	0.000134
480	18.88	18.40	0.48	0.0000543
720	18.88	18.40	0.48	0.0000362
1440	18.88	18.33	0.55	(0.0000206)
			Average,	0.0000748

$A_1K_1 = 0.00008$ and $K_1 = 0.0008$

Table XXIX.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N *n*-butyl chloride.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
120	18.58	17.48	1.10	0.000524
240	18.58	17.39	1.19	0.000283
480	18.58	16.87	1.71	0.000211
1440	18.58	15.74	2.84	(0.000125)
			Average,	0.000340

$A_1K_1 = 0.000365$ and $K_1 = 0.0036$

Table XXX.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isobutyl chloride.

t.	*A.*	*A*−*x.*	*x.*	*AK.*
120	18.88	18.66	0.22	(0.0000982)
440	18.88	18.58	0.30	0.0000336
720	18.88	18.58	0.30	0.0000224
1440	18.88	18.15	0.73	0.0000279
			Average,	0.000028

$A_1K_1 = 0.0000295$ and $K_1 = 0.00029$

Table XXXI.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N tertiary butyl chloride.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
120	18.88	18.27	0.61	(0.000277)
480	18.88	18.29	0.59	0.0000672
720	18.88	18.19	0.68	0.0000591
1440	18.88	18.06	0.82	0.0000308
			Average,	0.000052

A_1K_1 = 0.000055 and K_1 = 0.00055

Table XXXII.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N isoamyl chloride.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
60	18.88	18.60	0.28	(0.000250)
240	18.88	18.49	0.39	0.0000870
660	18.88	18.10	0.78	0.0000653
1440	18.88	17.40	1.48	(0.0000591)
			Average,	0.000071

A_1K_1 = 0.000075 and K_1 = 0.00075

Table XXXIII.

50°. 0.05 N 1-Phenyl-3-thiourazole + 0.05 N ethyl iodide.

t.	*A.*	*A*—*x.*	*x.*	*AK.*	K_1.
5	4.90	4.11	0.79	0.0384	
				A_1K_1=0.0392	1.568
10	4.90	3.57	1.33	0.0373	
				A_1K_1=0.0380	1.520
15	4.90	3.18	1.72	0.0360	
				A_1K_1=0.0367	1.468
31	4.90	2.46	2.44	0.0319	
				A_1K_1=0.0325	1.300
60	4.90	1.88	3.02	0.0268	
				A_1K_1=0.0273	1.096
120	4.90	1.29	3.61	0.0234	
				A_1K_1=0.0238	0.952
240	4.90	0.66	4.24	0.0268	
				A_1K_1=0.0273	1.096
5 mols. HCl. (sp. gr. 1.20)(0.388 cc.) added.					
60	4.71	3.54	1.17	0.0055	

Table XXXIV.

50°. 0.05 N 1-Phenyl-3-thiourazole + 0.05 N methyl iodide.

t.	*A.*	*A*—*x.*	*x.*	*AK.*	K_1.
3	4.90	2.05	2.85	0.463	
			A_1K_1=	0.472	18.88
5	4.90	1.40	3.50	0.500	
			A_1K_1=	0.510	20.40
10	4.90	0.90	4.20	0.444	
			A_1K_1=	0.453	18.12
15	4.90	0.75	4.15	0.369	
			A_1K_1=	0.377	15.04
30	4.90	0.67	4.23	0.210	
			A_1K_1=	0.214	8.56
60	4.90	0.93	3.97	0.0711	
			A_1K_1=	0.0725	2.90

Table XXXV.

25°. 0.05 N 1-Phenyl-3-thiourazole + 0.05 N ethyl iodide.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
60	4.71	3.69	1.02	0.00460
150	4.71	2.83	1.88	0.00443
			Average,	0.00451

A_1K_1 = 0.00479 and K_1 = 0.192

Table XXXVI.

Change of 1-Phenyl-3-thiourazole into the Disulphide.

50°. 0.05 N 1-Phenyl-3-thiourazole in 50 per cent alcohol.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
61	4.90	4.87	0.03	0.000101
150	4.90	4.82	0.08	0.000110
214	4.90	4.78	0.12	0.000116
300	4.90	4.68	0.22	0.0001085
390	4.90	4.64	0.26	0.000143
			Average,	0.00012

A_1K_1 = 0.00012 and K_1 = 0.0024

Table XXXVII.

50°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N sodium chloracetate in water solution.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
15	18.50	15.60	2.90	(0.0124)
30	18.50	12.00	6.50	0.0180
60	18.50	8.97	9.53	0.0177
120	18.50	6.14	12.36	0.0168

Average, 0.0175

A_1K_1 = 0.0189 and K_1 = 0.189

Table XXXVIII.

50°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N sodium chloracetate in 50 per cent alcohol.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
15	18.71	15.30	3.41	0.0148
30	18.71	13.13	5.58	0.0141
60	18.71	10.39	8.32	0.0133

Average, 0.0141

A_1K_1 = 0.015 and K_1 = 0.15

Table XXXIX.

25°. 0.2 N Sodium thioacetate + 0.2 N ethyl iodide.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
15	13.78	10.20	3.78	0.0252
30	13.78	7.41	6.37	0.0286
60	13.78	5.02	8.76	0.0290
120	13.78	2.54	11.24	(0.0368)
240	13.78	0.90	12.88	(0.0596)

Average, 0.027

A_1K_1 = 0.040 and K_1 = 0.40

Table XL.

50°. N Potassium hydroxide + N ethyl iodide.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
15	10.00	8.47	1.53	0.0120
30	10.00	7.49	2.51	0.0111
60	10.00	6.18	3.82	0.0103
120	10.00	4.37	5.63	0.0107

Average, 0.011

K_1 = 0.022

After the normal ethyl iodide in absolute alcohol had stood for forty-eight hours, 10 cc. were titrated with 0.1 N potassium hydroxide. 4.56 cc. were required. This showed that the ethyl iodide may be decomposed in the water and alcohol and accounts for the decrease in the velocity constant in the above table. See also Table XLIV.

Table XLI.

50°. N Potassium hydroxide and N ethyl iodide with 5 mols. KI (8.30 grams) added.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
15	10.00	8.99	1.01	0.00741
30	10.00	8.37	1.63	0.00648
60	10.00	7.50	2.50	0.00555
120	10.00	6.19	3.81	0.00512
			Average,	0.00614
			K_1	= 0.01228

Table XLII.

50°. N Potassium hydroxide + N methyl iodide.

	A.	*A*—*x.*	*x.*	*AK.*
4	10.00	7.05	2.95	0.104
8	10.00	5.69	4.31	0.0947
15	10.00	4.39	5.61	0.0852
32	10.00	2.99	7.01	0.0733
			Average,	0.0893
			K_1	= 0.1786

Table XLIII.

50°. N Potassium hydroxide and N methyl iodide with 5 mols. KI (8.30 grams) added.

t.	*A.*	*A*—*x.*	*x.*	*AK.*
4	10.00	8.40	1.60	0.0476
8	10.00	7.19	2.81	0.0382
15	10.00	5.91	4.09	0.0461
32	10.00	4.50	5.50	0.0381
			Average,	0.0425
			K_1	= 0.085

Table XLIV.

50°. Hydrolysis 0.5 N methyl iodide in 50 per cent alcohol.

t.	*A.*	$A-x$.	$K=\frac{1}{t}\log\frac{A}{A-x}$.
4	9.83	9.81	0.00022
9	9.83	9.77	0.00029
32	9.87	9.66	0.00024
90	9.87	9.42	0.00020
180	9.83	9.30	(0.00012)
240	9.83	8.67	0.00022
1440	9.83	6.51	(0.00012)
		Average,	0.00023

Table XLV.

The reaction between sodium phenyl-3-thiourazole and ethyl iodide was followed by means of conductivity measurements. Special experiments showed that the conductivity of the sodium urazole was not changed by the addition of the ethyl iodide. This shows that the ethyl iodide does not unite appreciably with the sodium or urazole ions.

25°. 0.2 N Sodium 1-phenyl-3-thiourazole + 0.2 N C_2H_5I in 50 per cent ethyl alcohol.

μv.	*t.*	Resistance.	*a.*	*b.*	*AK.*
15.48	0.0	102	54.70	45.30	....
16.52	2.9	102	56.30	43.70	0.0530
17.42	6.0	102	57.60	42.40	0.0728
17.90	11.3	60	45.10	54.90	0.0539
18.80	17.3	60	46.30	53.76	0.0620
19.95	30.2	60	47.80	52.20	0.0972
21.02	56.2	60	49.10	50.90	0.114
21.46	77.5	60	49.60	50.40	0.155
21.88	....	60	50.10	49.90	

It is evident that the method must be studied further in order to secure better constants. The conductivity data prove conclusively that only a very small amount of alkyl halide can be combined at any moment with the sodium or urazole ions.

Table XLVI.

25°. 0.1 N Sodium 1-phenyl-3-thiourazole + 0.1 N C_2H_5I in 50 per cent ethyl alcohol.

μ_v.	*t*.	Resistance.	*a*.	*b*.	*AK*.
17.62	0.0	140	48.10	51.90	.....
18.79	4.8	140	49.70	50.30	0.0309
20.52	13.3	140	51.90	48.10	0.0356
21.88	24.5	140	53.50	46.50	0.0366
22.87	31.6	140	54.60	45.40	0.0442
23.72	44.6	140	55.50	44.50	0.0470
24.30	59.6	140	56.10	43.90	0.0482
24.78	77.8	100	48.20	51.80	0.0496
26.63	....	100	50.00	50.00	.....

The method must be improved by further work.

Conclusions.

1. Work on the reactions of alkyl halides with urazoles, hydroxides, carbonates, thioacetates, etc., seems to prove that the alkyl halide reacts with the anion of the urazole, hydroxide, etc., according to the expression

$$C_2H_5I + \overline{OH} \longrightarrow C_2H_5OH + \overline{I},$$

or

$$\frac{dx}{dt} = K_{trans} \times C_{ethyl\ iodide} \times C_{OH}.$$

2. The alkyl halides do not seem to form alkyl derivatives of other substances through the intermediate dissociation into alkyl and halide ions, as Bruyn and Steger assumed:

$$KOH + C_2H_5I \rightleftharpoons \overset{+}{K} + \overline{OH} + \overset{+}{C_2H_5} + \overline{I} \longrightarrow C_2H_5OH + \overset{+}{K} + \overline{I}.$$

3. The experimental evidence is not in harmony with the view of Nef that alkyl halides react with compounds because the alkyl halide first dissociates into the corresponding halogen acid and an unsaturated methylene or olefine derivative, which then reacts with another substance:

$$C_2H_5I + \overset{+}{K} + \overline{OC_2H_5} \rightleftharpoons$$

$$CH_2C \rightleftharpoons + \overset{+}{H} + \overline{I} + \overset{+}{K} + \overline{OC_2H_5} \longrightarrow$$

$$CH_3CH \rightleftharpoons + HOC_2H_5 + \overset{+}{K} + \overline{I} \longrightarrow$$

$$CH_3CH_2—O—C_2H_5 + \overset{+}{K} + \overline{I}.$$

4. The alkyl halides do not seem to react with salts by first uniting with the cation and forming a complex cation which then reacts with the anion, as Euler assumed:

$$C_2H_5I + \overset{+}{K} + \overline{OH} \rightleftharpoons C_2H_5I.\overset{+}{K} + \overline{OH} \rightarrow C_2H_5OH + \overset{+}{K} + \overline{I}.$$

5. The alkyl halide seems to react as a neutral molecule with the anion of the substance which is alkylated, perhaps forming an unstable intermediate complex anion.

6. The alkyl iodides are more reactive towards the urazoles than are the alkyl bromides, and these in turn are more reactive than the alkyl chlorides. The primary alkyl halides are more reactive towards the urazoles than are the secondary alkyl halides, and these are more reactive than the tertiary alkyl halides. The so-called space interference seems to be effective in these reactions.

JOHNS HOPKINS UNIVERSITY,
June 1, 1907.

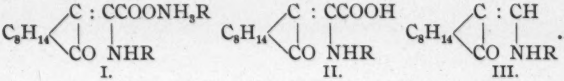
STUDY OF THE ACTION OF PRIMARY AND TERTIARY AMINES ON CAMPHOROXALIC ACID.

[XII. COMMUNICATION ON CAMPHOROXALIC ACID.[1]]

BY J. BISHOP TINGLE AND L. F. WILLIAMS.

THEORETICAL.

In a series of papers by J. Bishop Tingle and his co-workers it has been shown that camphoroxalic acid combines with a number of primary amines to form condensation products which usually belong to the three types,



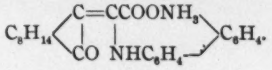
I. II. III.

In the case of some amines which contain more than one amino group, such as benzidine,[2] the compound, though ap-

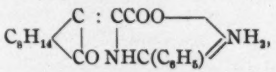
[1] The other papers relating to this subject have been published as follows: Inaug. Diss., Munich, 1889, p. 34; J. Chem. Soc., **57**, 652 (1890); THIS JOURNAL, **19**, 393 (1897); **20**, 318 (1898); **21**, 238 (1899); **23**, 214 (1900); J. Am. Chem. Soc., **23**, 363 (1901). THIS JOURNAL, **34**, 217 (1905); **36**, 223 (1906); J. Am. Chem. Soc., **29**, 1242 (1907); THIS JOURNAL, **39**, 105 (1908).

[2] THIS JOURNAL, **34**, 231 (1905).

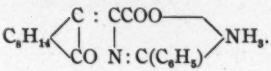
parently different from the above typical forms, is probably fundamentally similar, one amino group condensing and one neutralizing the carboxyl, as expressed by the formula



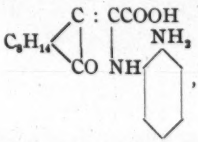
The product formed with benzamidine[1] is probably essentially similar in constitution,



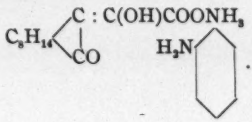
or



In the case of orthophenylenediamine[2] another complication is encountered. It is evident that a compound of type II,



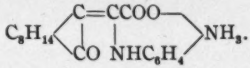
would be extremely likely to combine further to form a five-membered ring, and that the same would, of course, be true if the amino group first attacked the carboxyl, as in the case of a substance with the structure



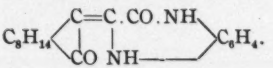
Experiment showed that this actually took place because, in spite of many attempts to do so, it was not found to be possible to isolate any compound corresponding to either

[1] This Journal, **34**, 230 (1905).
[2] J. Amer. Chem. Soc., **23**, 375 (1901).

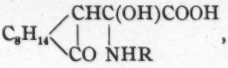
of the two formulae given above, or to such a substance as is represented by the expression



The compound which was actually obtained, as the result of a number of experiments carried out under very varied conditions, was the quinoxaline derivative,



The formation, primarily, in all these cases, of an addition compound,



is, of course, assumed. A number of such additive products from primary amines have been definitely isolated and studied by the senior author, alone, and in conjunction with Alfred Tingle, W. E. Hoffman, Jr., and C. J. Robinson.[1]

Their constitution and the bearing which their formation has on the ketonic-enolic question have been fully considered and discussed.[2] A number of addition compounds of camphoroxalic acid and secondary amines have been described by Bishop Tingle and W. E. Hoffman, Jr.,[3] and also by the present authors.[4]

Returning, now, to the substances belonging to the three types formulated above, there are two points which call for comment. A given amine is not necessarily capable of forming compounds belonging to each of these classes; some can do so, others only yield two, and certain amines appear to be able to give not more than one of them; in this latter event it is usually the substance belonging to type three which is formed. We shall return to this point after presenting our own results.

[1] *Loc. cit.*
[2] *Vide*, especially, THIS JOURNAL, **36**, 223 (1906).
[3] *Ibid.*, **34**, 217 (1905).
[4] *Ibid.*, **39**, 122 (1908). Cf. O. Dimroth: Ber. d. chem. Ges., **40**, 2404 (1907).

An inspection of the amines hitherto employed for the condensations discloses the fact that a considerable number have failed to react at all with camphoroxalic acid. It is obvious that the cause of this failure must be cleared up before it will be possible to formulate the regularity underlying the reactions in question. Further, it is desirable to increase the available data by extending the experiments so as to include a larger number of amines within the scope of the investigation. This was, therefore, our first object in undertaking the investigation whose results are recorded in the present paper.

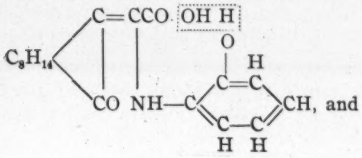
The readiness with which aniline reacts with camphoroxalic acid,[1] and the difficulty experienced in obtaining condensation products with paranitraniline, on the one hand, and with para- and metaphenylenediamine[2] on the other, made it desirable to investigate the behavior of the aminophenols in this connection, because these latter compounds might be regarded as being in a position midway between the substances in question. They are less basic than aniline, but more so than the nitranilines. They are disubstituted compounds like the nitranilines and phenylenediamines, but, in the case of the aminophenols, a condensation, in addition to salt formation, is highly improbable. This latter point is of some importance, because it has been shown by Bishop Tingle, in conjunction, with Messrs. Cram[3] and Lovelace,[4] that salt formation is, in some cases, an important factor in promoting intramolecular condensations.

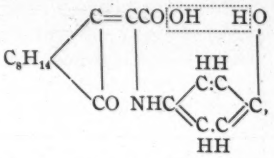
The objection might be raised that there is nothing to prevent the aminophenols from first forming salts which could afterwards undergo rearrangement and condensation. The answer to this is found in the work of Bishop Tingle and Alfred Tingle[5] on the compounds of aniline and camphoroxalic acid, and especially in their results with *o*-phenylenediamine. They found that this base gave the compound mentioned

[1] THIS JOURNAL, **21**, 238 (1899).
[2] *Ibid.*, **34**, 253 (1905).
[3] *Ibid.*, **37**, 596 (1907).
[4] *Ibid.*, **38**, 642 (1907).
[5] *Loc. cit.*

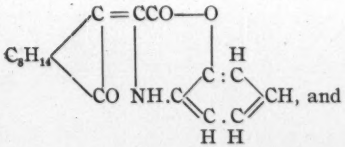
above, alike from the free acid, its sodium salt, or from ethyl camphoroxalate. The same point is demonstrated by our own results with benzalaniline and camphoroxalic acid, cf. p. 285.

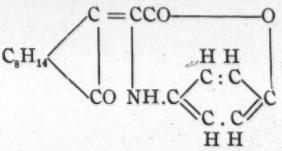
Assuming, then, that the amino groups of ortho- and para-aminophenol combine in the regular manner with camphoroxalic acid, it is at least conceivable that the resulting substances,





might eliminate the elements of water, as shown by the dotted lines in the preceding formulae or in some other manner, giving rise, finally, to the compounds





Clearly, such a double condensation, if it could occur at all, would, doubtless, depend essentially on the possibility

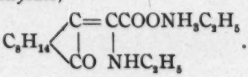
of forming new cycloids of the maximum stability, *i. e.*, those containing five or six members. As will be seen from the second part of this paper, these ideas have been realized in the case of orthoaminophenol, whereas, in the case of the para compound, two molecules combined with one of the acid, the product being a salt of an addition product.

In connection with another line of work, it appeared to be desirable to investigate the behavior of camphoroxalic acid toward certain *tertiary bases*, especially those of an alkaloidal nature, the particular object being to obtain salts with well developed crystallizing power, which might ultimately prove of service in the examination of camphoroxalic acid for possible stereo- or structural isomers. Our results in this connection are discussed later in this present paper.

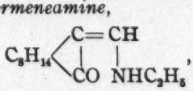
In previous communications on this subject[1] the interaction of camphoroxalic acid with methylamine, α-naphthylamine, β-naphthylamine, paratoluidine, metatoluidine, benzylamine, benzamidine, benzidine, 1,2,4-nitrotoluidine, orthophenylenediamine, aniline, semicarbazine, dimethylamine, diethylamine, hydroxylamine, ammonia, phenylhydrazine, urea, methylurea, symmetrical dimethylurea, unsymmetrical dimethylurea, hydrazine, and parabromphenylhydrazine has been studied. We have now supplemented this by the investigation of the following substances:

Primary Amines.

1. *Ethylamine.*—Ethylamine gives *ethylamine ethylcamphoformeneaminecarboxylate*,



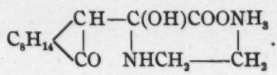
When this salt is heated considerably above its melting point, *ethylcamphoformeneamine*,



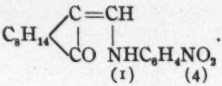
is formed.

[1] *Loc. cit.*

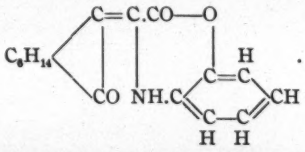
2. *Ethylenediamine.*—Ethylenediamine gives a product resembling the direct addition products of primary amines with this acid which have been described by Bishop Tingle and his colleagues,[1] and is, accordingly, a *camphoformolamine derivative*, represented by the formula



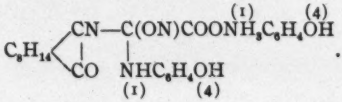
3. *Paranitraniline.*—Paranitraniline gives *paranitrophenylcamphoformeneamine*,



4. *Orthoaminophenol.*—Orthoaminophenol gives the lactone of *orthohydroxyphenylcamphoformeneaminecarboxylic acid*,



5. *Paraminophenol.*—Paraminophenol gives *paraminophenol parahydroxyphenylcamphoformolaminecarboxylate*,



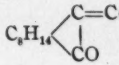
Attempts were made to obtain compounds of camphoroxalic acid with *n-propylamine* (6), *metaphenylenediamine* (7), and *paraphenylenediamine* (8), but without success. Reaction appears to take place in each case, but the products cannot be purified by any of the ordinary methods. Even had it

[1] *Loc. cit.*

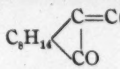
been worth while, time was lacking to devise a special mode of isolation for each compound.

Tertiary Amines.

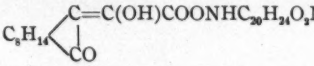
9. *Trimethylamine.*—Trimethylamine gives *trimethylamine camphoroxalate*,



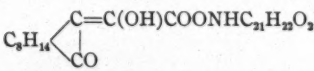
10. *Triethylamine.*—Triethylamine yields *triethylamine camphoroxalate*,



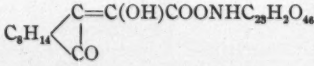
11. *Quinine.*—Quinine forms *quinine camphoroxalate*,



12. *Strychnine.*—Strychnine gives *strychnine camphoroxalate*,

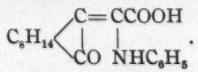


13. *Brucine.*—Brucine yields *brucine camphoroxalate*,



Attempts to prepare two isomeric compounds were unsuccessful.

14. *Benzalaniline.*—Benzalaniline gives *phenylcamphoformeneaminecarboxylic acid*,



Its production is evidently due to a hydrolysis of the benzalaniline into benzaldehyde and aniline under the influence of the acid and of a trace of water in the reacting materials.

As the reaction proceeded the quantity of water would, of course, increase steadily, because it is necessarily formed as a result of the condensation. The presence of benzaldehyde among the products of the reaction was proved by its odor.

The formation of the above condensation product demonstrates once more, in the clearest manner, the superior reactivity of the enolic group C : COH, as compared with the carboxylic group, *i. e.*, even with relatively strong bases, if other conditions are favorable, condensation, rather than salt formation, takes place. Cf. p. 280.

15. *Piperine.*—Piperine gave only a small amount of piperic acid, owing, probably, to the presence of a little moisture in the reagents.

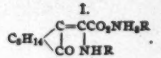
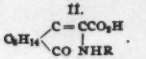
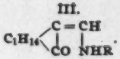
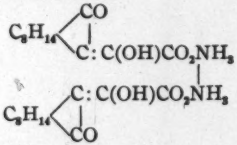
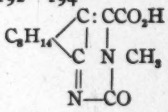
16. *Tribenzylamine.*—Attempts to obtain a crystalline salt of tribenzylamine and camphoroxalic acid were unsuccessful.

It is evident that, of the salts described above, those of brucine and strychnine appear to be admirably adapted for the investigation of possible isomeric forms of camphoroxalic acid. This matter will receive attention in the near future.

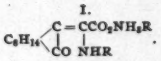
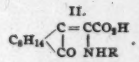
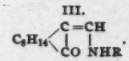
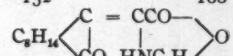
17. *Tetraethylammonium Hydroxide.*—Tetraethylammonium hydroxide gave a crystalline *salt*, but it was too unstable to permit of complete purification.

The following table (pp. 286–7) shows the various condensation compounds of camphoroxalic acid and primary amines which have been prepared by Bishop Tingle and his coworkers[1] and also those which are described for the first time in this paper. The former are indicated by an asterisk (*). Those marked + contain the elements of 1 molecule of water more than is shown by the type formula. When no definite compound could be isolated the space in the table is occupied by a dash.

[1] *Loc. cit.*

	Primary amine.	I. 	II. 	III. 
1	NH_2	.....	*178°	.....
2	NH_2OH	.....	+*146°.5	.....
3	CH_3NH_2	*172°	.....	*131°
4	$C_2H_5NH_2$	109°	.....	118°
5	n-$C_7H_7NH_2$	Gum was formed		
6	H_2NNH_2			*186°
7	$OC(NH_2)_2$	*192°–194°		
8	$CH_3NHCONH_2$			*154°
9	$(CH_3)_2NCONH_2$	.....	.....	.....
10	$H_2NCH_2CH_2NH_2$	.....	+220°	.....
11	$H_2NCONHNH_2$	.....	*198°	.....
12	$C_6H_5CH_2NH_2$	*147°.5	*140°	*96°.5
13	$C_6H_5NH_2$	*158°	*174°	*166°
14	$CH_3C_6H_4NH_2$(1:2)	.....	.....	.....

1.39
908

	Primary amine.	I. 	II. 	III. 
15	$CH_3C_6H_4NH_2$(1:3)	*126°	*154°	.....
16	$CH_3C_6H_4NH_2$(1:4)	*152°	*168°	*178°
17	$HOC_6H_4NH_2$(1:2)			*159°.5
18	$HOC_6H_4NH_2$(1:4)	+190°	178°	314°
19	$C_6H_4(NH_2)_2$(1:2)	$C_{18}H_{22}O_2N_2$	*246°	.....
20	$C_6H_4(NH_2)_2$(1:3)	.....	.....	.....
21	$C_6H_4(NH_2)_2$(1:4)	.....	.....	.....
22	$O_2NC_6H_4NH_2$(1:4)	.....	.....	156°
23	$CH_3COC_6H_4NH_2$(1:4)	.....	.....	.....
24	$CH_3C_6H_3(NO_2)NH_2$(1:2:4)	.....	.....	*192°
25	$C_6H_5NHNH_2$	.....	*120°	.....
26	$BrC_6H_4NHNH_2$(1:4)	.....	+*149°	.....
27	$C_6H_5C(:NH)NH_2$	$C_{19}H_{24}O_2N_2$	*184°	.....
28	$H_2NC_6H_4C_6H_4NH_2$(1:4)			*190°
29	α-$C_{10}H_7NH_2$	*165°	*170°	.....
30	β-$C_{10}H_7NH_2$	*169°	*172°.5	*173°

Experimental.

In the preparation of camphoroxalic acid the method used was that described by J. Bishop Tingle and W. E. Hoffman, Jr.,[1] with the changes which were suggested and employed by J. Bishop Tingle and C. J. Robinson.[2]

Primary Amines.

1. *Ethylamine.*—Ethylamine (5 grams = 2 mol.) and camphoroxalic acid (12.5 grams = 1 mol.) were placed in a pressure bomb with 30 cc. of absolute ethyl alcohol and heated to 100° for six hours. The bomb was opened after cooling and the excess of solvent evaporated. A semicrystalline mass was left which, on dissolving in gasoline and adding chloroform, separated from the solution in a fairly pure condition. The compound was purified by recrystallization from ethyl acetate, being deposited in white needles, which melt at 109°. When dissolved in alcohol and ferric chloride is added, no color is produced. Analysis showed the compound to be *ethylamine ethylcamphoformeneaminecarboxylate.*

Analysis:

0.2303 gram substance gave 19.2 cc. N at 24° and 760 mm.

	Calculated for $C_8H_{14}\begin{cases} C=CCOONH_3C_2H_5 \\ CO\ NHC_2H_5 \end{cases}$	Found.
N	9.47	9.13

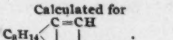
When treated with sodium hydroxide the above salt dissolves but, on acidification with dilute hydrochloric acid, decomposes into camphoroxalic acid and ethylamine.

When heated at 150° *ethylamine ethylcamphoformeneaminecarboxylate* gives off carbon dioxide and ethylamine and forms a compound which, when recrystallized from acetone, is deposited in semitransparent plates, melting at 118°. With alcoholic ferric chloride no color reaction is produced. Analysis proved this compound to be *ethylcamphoformeneamine.*

[1] THIS JOURNAL, **34**, 235 (1905).
[2] *Ibid.*, **35**, 248 (1906).

Analysis:

0.1135 gram substance gave 7.0 cc. N at 24° and 755 mm.

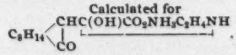


	Calculated for	Found.
N	6.77	6.70

2. *Ethylenediamine.*—The free base was prepared as follows: Ethylenediamine hydrochloride (5 grams = 1 mol.) was dissolved in absolute methyl alcohol. To this was added an alcoholic solution of potassium hydroxide containing 42 grams = 2 mol. The alcoholic solution of the base was filtered from the potassium chloride and to the solution camphoroxalic acid (8.4 grams = 1 mol.) was added and the liquid heated for a short time. Crystals began to form and the solution was concentrated further in a vacuum desiccator. The compound was purified by crystallization from a mixture of 60 parts of methyl alcohol and 40 parts of water, being deposited in greyish-white, microscopic crystals, melting at 220°. It is sparingly soluble in ethyl acetate, acetone, benzene, toluene, ether, and in ethyl and methyl alcohols. Analysis showed the substance to be an additive compound similar to the body obtained by Bishop Tingle[1] from hydroxylamine and camphoroxalic acid, and it belongs to the *camphoformolamine series.*

Analysis:

0.1816 gram compound gave 15.3 cc. N at 770 mm. and 20°.



	Calculated for	Found.
N	9.87	9.58

When the above compound is heated at 215° water and carbon dioxide are given off and a dark gummy mass is left in the tube. A semicrystalline mass was separated from this but no crystals free from gum could be obtained, so that no attempt was made to analyze the compound. The gummy mass gave no color reaction with alcoholic ferric chloride.

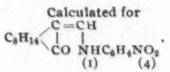
[1] *Loc. cit.*

3. *Paranitraniline.*—Paranitraniline (4.15 grams = 1 mol.), camphoroxalic acid (6.75 grams = 1 mol.), and benzene (30 cc.) were heated, under pressure, at 135°-140°, for six hours. When the bomb was opened, after cooling, there was considerable internal pressure. The benzene was evaporated and a tarry mass was formed. As no crystals could be separated from this tar by dissolving it in various solvents, it was treated with a dilute aqueous solution of sodium carbonate. The part insoluble in the carbonate solution was dissolved in benzene and ligroin was added. Crystals separated and were further purified by recrystallization from alcohol, being deposited as glistening, brownish-yellow needles, melting at 156°. Analysis of this compound showed it to be *paranitrophenylcamphoformeneamine.*

Analysis:

I. 0.1737 gram substance gave 14.8 cc. N at 761 mm. and 19.5°.

II. 0.1108 gram substance gave 0.2772 gram CO_2 and 0.0665 gram H_2O.



	Calculated for $C_8H_{14}C{=}CH\,CO\,NHC_6H_4NO_2$ (1) (4)	Found. I.	II.
C	68.00	....	68.23
H	6.66	....	6.66
N	9.33	9.61	....

With alcoholic ferric chloride no color reaction is obtained.

On acidification of the sodium carbonate solution mentioned above with dilute hydrochloric acid, camphoroxalic acid is deposited.

4. *Orthoaminophenol.*—Orthoaminophenol hydrochloride (5.8 grams = 2 mol.) and camphoroxalic acid (4.5 grams = 1 mol.) were heated in alcoholic solution until crystals began to form. These were purified by recrystallization from ethyl acetate, being deposited in well-defined yellow crystals belonging to the monoclinic system and melting at 159°.5. Analysis of this compound showed it to be the *lactone* of *orthohydroxyphenylcamphoformeneaminecarboxylic acid.*

Analysis:

I. 0.1277 gram substance gave 0.0772 gram H_2O and 0.3413 gram CO_2.

II. 0.1871 gram substance gave 8.2 cc. N at 750 mm. and 20°.

	Calculated for $C_8H_{14}\langle \overset{C=CCOO}{\underset{CO\ NH-C_6H_4}{|\ \ |}}$	Found. I.	Found. II.
C	72.67	72.89	....
H	6.45	6.71	....
N	4.72	....	4.85

The compound is practically insoluble in water, readily soluble in barium hydroxide solution, and slightly soluble in sodium carbonate solution.

When heated to 290° the substance sublimes, forming long, silky, yellow needles which have the same melting point as the original crystals, *i.e.*, 159°.5. On heating the compound with one molecular proportion of barium oxide at 290° for forty-five minutes, a tarry mass was formed from which no crystals could be obtained. Some of the compound described above was dissolved in aqueous barium hydroxide solution and boiled for five minutes, then a little alcohol was added and the solution allowed to stand overnight. It was then acidified with dilute hydrochloric acid and crystals separated. After washing them with water and drying, they melted at 155°-157°, and on recrystallizing the compound once from ethyl acetate the product melted at 159°.5, showing that this treatment with alkali has caused no change. The substance is, therefore, evidently a lactone.

With alcoholic ferric chloride no color reaction was produced.

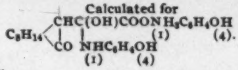
5. *Paraminophenol.*—Paraminophenol (5 grams = 2 mol.), camphoroxalic acid (5 grams = 2 mol.), and absolute alcohol (40 cc.) were heated under pressure for two hours, at 105°-110°. A few crystals had separated on cooling, and a further portion was obtained on concentrating the solution. Recrystallization from alcohol caused the compound to be deposited in light, yellow, feathery crystals, melting at 190° and decomposing when heated above the melting point. Analysis of

this substance showed it to be *paraminophenol parahydroxy phenylcamphoformolaminecarboxylate.*

Analysis:

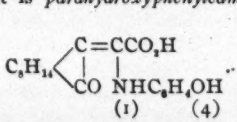
I. 0.1083 gram substance gave 0.2587 gram CO_2 and 0.0708 gram H_2O.

II. 0.1647 gram substance gave 9.1 cc. N at 761 mm. and 23°.

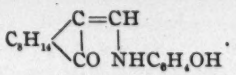


	Calculated for	Found. I.	Found. II.
C	65.11	65.14	....
H	6.83	7.26	....
N	6.34	....	6.09

When the compound described above is heated for a short time with dilute hydrochloric acid, the crystals become yellow but do not go into solution. Purified by crystallizing from benzene, the compound melts and decomposes at 178°. No analysis was made of this substance, but from the mode of formation and its properties there can hardly be any doubt that it is *parahydroxyphenylcamphoformeneaminecarboxylic acid,*



When this acid is heated above its melting point, carbon dioxide is eliminated and a gum is left which, after solution in benzene, separates in greyish, microscopic crystals, softening at 305° and melting at 314°. From its mode of formation this compound is evidently *parahydroxyphenylcamphoformeneamine,*



6. *Propylamine.*—Propylamine and camphoroxalic acid were mixed in the proportion of 2 molecules of the amine to 1 of the acid and heated in alcoholic solution, so as to prepare a condensation compound. A gummy mass was formed from which no definite compound could be isolated. Sodium cam-

phoroxalate was also tried with propylamine in alcoholic solution but with no better results. These experiments were made before our work[1] on secondary amines was completed.

In view of some of the results with aliphatic amines which are described in that paper, there can be little doubt that propylamine and camphoroxalic acid condense to form a liquid compound which could probably be purified by distillation under diminished pressure. Unfortunately there was no time to test this idea.

7. *Metaphenylenediamine.*—Attempts to prepare condensation compounds with this amine and camphoroxalic acid were carried out as follows: The amine hydrochloride (1 mol.), camphoroxalic acid, (1 mol.), and potassium hydroxide (2 mol.) were heated under pressure with absolute alcohol at 130° for 5 hours. After freeing the solution from the potassium chloride formed, it was attempted to purify the crystals separating from the alcohol by using various solvents, but they were contaminated with inorganic matter from which they could not be freed. Consequently they gave no definite melting point and no concordant analytical results.

8. *Paraphenylenediamine.*—The experiments with this compound were made in a similar manner to those with the meta derivative, the results being essentially the same. There is no doubt that, in both cases, a reaction takes place. The compounds which are likely to have been formed are not, however, at present of sufficient importance to us to justify the large expenditure of time and material which would be needed for their isolation, consequently the matter was not pursued further.

Tertiary Amines.

9. *Trimethylamine.*—Trimethylamine hydrochloride (4 grams = 1 mol.) was dissolved in absolute methyl alcohol. To this was added potassium hydroxide (2.35 grams = 1 mol.), also in absolute methyl alcohol solution, to liberate the base. The potassium chloride was separated and to the solution camphoroxalic acid (9.5 grams = 1 mol.) was added.

[1] THIS JOURNAL, 39, 105 (1908).

Without further heating the alcohol was evaporated over sulphuric acid in a vacuum desiccator. The resulting compound was purified by crystallization from benzene, being deposited in white, microscopic crystals melting and evolving gas at 139°–140°. With alcoholic ferric chloride a violet color is produced. The compound dissolves in aqueous sodium bicarbonate solution with evolution of gas. Analysis showed the substance to be *trimethylamine camphoroxalate.*

Analysis:

0.1833 gram substance gave 7.9 cc. N at 24°.5 and 771 mm.

	Calculated for $C_8H_{14}\begin{cases}C:C(OH)COONH(CH_3)_3\\ \vert \\ CO\end{cases}$	Found.
N	4.95	4.77

When the preceding compound is heated above its melting point a gum is formed from which it was impossible to isolate a crystalline derivative.

Triethylamine.

10. Triethylamine.—Triethylamine hydrochloride (2 grams = 1 mol.), camphoroxalic acid (3.3 grams = 1. mol.), and potassium hydroxide (0.8 gram = 1 mol.) were mixed and heated in absolute ethyl alcohol. A precipitate of potassium chloride was formed and was separated from the solution, which was then concentrated. The resulting solid was dissolved in benzene and ligroin added. On standing, crystals separated. These were recrystallized several times from benzene, being deposited in small, white needles melting at 102°–103°. With alcoholic ferric chloride, a violet color is produced. The compound dissolves in aqueous sodium carbonate solution with the evolution of gas. As the yield was small, the reaction was repeated under conditions similar to those with trimethylamine, whereupon the yield was very good. Analysis of this compound showed it to be *triethylamine camphoroxalate.*

Analysis:

0.1702 gram substance gave 6.6 cc. N at 23°.5 and 767 mm.

	Calculated for $C_8H_{14}\begin{cases}C:C(OH)COONH(C_2H_5)_3\\ \vert \\ CO\end{cases}$	Found.
N	4.31	4.27

When this compound is heated above its melting point a gummy mass is formed which, when dissolved in ethyl acetate, deposits crystals, but these could not be obtained with a definite melting point, nor could concordant analyses of them be made.

11. Quinine.—Quinine (5 grams = 1 mol.) and camphoroxalic acid (4 grams = 1 mol.) were dissolved in benzene. The solution was then allowed to remain at the ordinary temperature for 24 hours. At the end of this time the crystals had separated. These were purified by crystallization from ether, being deposited as white, microscopic crystals melting and evolving gas at 160°–161°. With alcoholic ferric chloride solution a violet color is produced. Analysis showed the compound to be *quinine camphoroxalate.*

Analysis:

I. 0.1403 gram substance gave 0.3605 gram CO_2 and 0.0951 gram H_2O.

II. 0.2028 gram substance gave 9.2 cc. N at 25°.5 and 755 mm.

	Calculated for $C_8H_{14}\begin{matrix}C:C(OH)COONHC_{20}H_{24}O_2N\\ CO\end{matrix}$	Found. I.	Found. II.
C	70.02	70.07	....
H	7.35	7.53	....
N	5.12	....	4.88

When this salt is heated above its melting point a gum is formed, from which no crystals could be obtained. This gum was treated with an aqueous sodium carbonate solution and extracted with ether. Free quinine was isolated from the ethereal solution and, on acidifying the sodium carbonate solution with dilute hydrochloric acid, camphoroxalic acid separated.

12. Strychnine.—Strychnine (5 grams = 1 mol.) and camphoroxalic acid (3.4 grams = 1 mol.) were dissolved in benzene and allowed to stand at room temperature for 18 hours. Crystals were formed and these were purified by recrystallization from ethyl acetate, being deposited as small, white needles melting and evolving gas at 214°–215°. With alco-

holic ferric chloride solution a violet color is produced. Analysis showed this compound to be *strychnine camphoroxalate* and that it crystallizes with 0.5 molecule of ethyl acetate.

Analysis:

I. 0.2420 gram substance gave 0.6147 gram CO_2 and 0.1556 gram H_2O.

II. 0.1884 gram substance gave 7.8 cc. N at 23°.5 and 763 mm.

III. 0.7691 gram substance lost 0.0513 gram on heating at 104°.

	Calculated for $C_9H_{14}\langle^{C:C(OH)COONH}_{CO}\rangle NO_2H_{22}C_{21}$	Calculated for $C_9H_{14}\langle^{C:C(OH).COONH}_{C}\rangle NO_2H_{22}C_{21}$ $+0.5\ CH_3COOC_2H_5$.	Found. I.	Found. II.
C	70.91	69.10	69.27	....
H	6.85	7.18	7.14	....
N	5.02	4.75	....	4.62

Calculated for 0.5 $CH_3COOC_2H_5$.	Found. III.
6.79	6.67

When the preceding compound is heated above its melting point the odor of camphor is quite noticeable on opening the tube. After removal of the camphor a gum is left from which no crystalline derivative could be isolated.

13. Brucine.—With brucine and camphoroxalic acid it was attempted to obtain two isomeric compounds, and with this end in view the reaction was carried out as follows:

Brucine (2.5 grams = 0.5 mol.) was dissolved in hot benzene. To this camphoroxalic acid (2.8 grams = 1 mol.) was added. The solution was allowed to cool and crystals were soon deposited. These were filtered off and to the solution a second quantity of brucine (2.5 grams = 0.5 mol.) was added, the liquid being heated to dissolve the brucine. On cooling, crystals were formed. These were separated and were found to be identical with the first portion. The compound was purified by recrystallization from alcohol, being deposited in small, glistening, white plates melting and evolving gas at

235°–236°. The substance gives a violet color with alcoholic ferric chloride solution. Analysis of the compound proved it to be *brucine camphoroxalate.*

Analysis:

0.1822 gram substance gave 7.7 cc. N at 24°.5 and 764 mm.

	Calculated for $C_8H_{14}\langle^{C:O(OH)COONHC_{23}H_{26}O_4N}_{CO}$	Found.
N	4.54	4.63

This shows that brucine, as well as quinine and strychnine, readily forms salts with camphoroxalic acid and that, under the conditions employed, no isomeric derivatives are produced. This matter will receive further attention subsequently.

When the brucine salt is heated above its melting point, water and carbon dioxide are given off and the odor of camphor is very pronounced. A gummy mass is left in the tube, from which no crystals could be isolated by the use of ordinary solvents. The gum was treated, finally, with dilute sodium carbonate solution and extracted with ether. A very small amount of material was dissolved in the ether. Some of it, which did not dissolve in the carbonate solution, was recrystallized and found to be impure brucine. On acidifying the carbonate solution with dilute hydrochloric acid a small amount of camphoroxalic acid separated. Evidently the salt had decomposed under the conditions of the heating and subsequent treatment.

14. Benzalaniline.—Benzalaniline (4 grams = 1 mol.), camphoroxalic acid (5 grams = 1 mol.), and absolute alcohol (30 cc.) were heated under pressure at 120°, for two hours. On evaporating the alcohol a gummy mass was left, but when this was dissolved in benzene and ligroin was added, crystals separated. These were purified by recrystallization from benzene, separating as yellow, microscopic crystals melting at 174°. Analysis showed this compound to be *phenylcamphoformeneaminecarboxylic acid.*

Analysis:

I. 0.1035 gram substance gave 0.2740 gram CO_2 and 0.0734 gram H_2O.

II. 0.1807 gram substance gave 7.8 cc. N at 22° and 762 mm.

	Calculated for $C_6H_{14}\begin{cases}C=CCOOH\\ CO\ NHC_6H_5\end{cases}$	Found. I.	II.
C	72.24	72.20	....
H	7.02	7.87	....
N	4.68	....	4.79

This compound was found to be identical with that prepared by Bishop Tingle[1] from aniline and camphoroxalic acid. Comparative melting points were made on the compound from benzalaniline and aniline by using three capillary tubes, containing, respectively, the compounds from benzalaniline, and from aniline, and a mixture of the two. The three tubes were heated at once and the substance in each melted at the same point, namely, 174°. As has been pointed out before, such comparisons are necessary to establish the identity of many compounds of this series, because the melting point depends greatly on the rapidity with which the substances are heated. It is evident that, under the conditions employed, benzalaniline is hydrolyzed to its constituents, the aniline combining with the camphoroxalic acid and the benzaldehyde remaining in the free state. The bearing of this fact on the general course of the condensation of camphoroxalic acid with bases is pointed out in the theoretical portion of this paper.

Another attempt to prepare a condensation product from camphoroxalic acid and benzalaniline was made as follows:

Benzalaniline (5.5 grams = 1.5 mol.), sodium camphoroxalate (5 grams = 1 mol.), and 40 cc. of anhydrous benzene, which had been dried over sodium, were heated under pressure for four hours, at 105°–108°. When the benzene was evaporated in a vacuum desiccator over sulphuric acid, a gummy mass was left. As no crystals could be separated by dissolving the product in ordinary solvents, it was dissolved

[1] This Journal, **21**, 238 (1899).

in alcohol and acidified with dilute acetic acid. After being freed from the sodium acetate, the solution was concentrated and a gum was formed. This was dissolved in benzene and sodium carbonate added. On acidifying the sodium carbonate solution with dilute hydrochloric acid, a yellow precipitate was deposited. This was purified by recrystallizing from benzene and was found to be identical with the compound obtained in the former experiment.

15. Piperine.—Piperine (7.1 grams = 1 mol.), camphoroxalic acid (6.7 grams = 1 mol.), and benzene (60 cc.) were heated under pressure at 165° for five hours. Some crystals had separated when the bomb was opened.

These were recrystallized from alcohol and were deposited in light yellow needles, softening at 210° and melting at 217°. The color, form, and melting point of these crystals correspond exactly with those of piperic acid.

On concentrating the solution from the bomb, crystals were deposited. These were recrystallized from alcohol and were found to be unchanged piperine.

An analysis for nitrogen was made with the compound before its nature was known but, of course, none was found.

The piperic acid was formed in very small quantity. Its production is doubtless due to traces of moisture in the materials and vessel used in the experiment.

16. Tribenzylamine.—Tribenzylamine and camphoroxalic acid were heated, in alcoholic solution, on the water bath, and a gum was formed from which we were unable to isolate a crystalline compound with a definite melting point. A semicrystalline mass was separated from the gum, but it could not be obtained in a pure condition. On treating this with sodium carbonate and extracting with ether, free tribenzylamine was obtained from the ethereal solution. The sodium bicarbonate solution was acidified with dilute hydrochloric acid and camphoroxalic acid separated, showing that the treatment with carbonate had decomposed the semicrystalline mass. The latter must, therefore, have consisted of *tribenzylamine camphoroxalate.*

17. Tetraethylammonium Hydroxide. — Tetraethylammonium hydroxide, 10 per cent aqueous solution, and camphoroxalic acid were mixed in 95 per cent alcohol and heated for a short time. The alcohol was allowed to evaporate spontaneously and the residue was crystallized from benzene, being deposited in glistening white needles. These give a violet color with ferric chloride solution. Attempts were made to analyze this compound, but it decomposes so easily that no concordant results could be obtained. It is, doubtless, *tetraethylammonium camphoroxalate.*

We desire to express our grateful thanks to the Trustees of the Warren Research Fund of the American Academy of Arts and Sciences for a grant to defray a part of the cost of some of the chemicals used in the investigation recorded in the preceding pages.

The work described in this paper has been carried out at the Johns Hopkins University. It will be continued by the senior author at this university.

McMaster University,
Toronto, Canada,
July, 1907.

ON THE REACTIONS OF CARBONYL COMPOUNDS WITH HYDROXYLAMINE AND HYDROXYLAMINE HYDROCHLORIDE.

[SEVENTH COMMUNICATION ON CATALYSIS.[1]]

By S. F. Acree.

(The writer is indebted to the Carnegie Institution of Washington for aid in this work.)

The recent articles by Abel,[2] Lapworth,[3] Landrien,[4] and Euler[5] bear so directly on our investigations on catalysis which are being conducted in this laboratory that the writer wishes to record the following comments:

[1] Acree and Hinkins: This Journal, **25**, 370; Dental Cosmos, June, 1901. Acree and Johnson, This Journal, **27**, 410; **28**, 258. Acree and Nirdlinger: *Ibid.*, **28**, 489. Acree, Johnson, and Nirdlinger: *Ibid.*, **28**, 746.

[2] Z. Elek. Chem., **13**, 555.

[3] J. Chem. Soc., **91**, 1133.

[4] Compt. rend., **140**, 1392.

[5] Z. physiol Chem., **52** 146.

Abel showed that the apparently noncatalyzed reaction between hydrogen peroxide and thiosulphates proceeds with *measurable* rapidity. The reaction velocity is increased by the presence of iodide ions because the hydrogen peroxide, reacting with them with a measurable velocity, forms a small amount of the iodoso ion, which reacts with immeasurable rapidity with the thiosulphate and hydrogen ions.

The work of Abel is certainly of the very greatest importance as it gives us another example in which the purely catalytic reactions, as defined by Ostwald,[1] such as inversion of cane sugar, hydrolysis of esters by acids, etc., are connected with the clear-cut cases of catalytic changes through reactions of measurable amounts of intermediate products formed by the reaction or union of the catalyzer with some other substance present. The discovery of other similar cases is very much to be desired. To Abel's list of such catalytic reactions through measurable amounts of intermediate products should be added the work of Stieglitz[2] on the hydrolysis of imidoester cations, that of Acree and Johnson[3] and of Acree and Shadinger[4] on the negative catalysis which is produced by the influence of hydrogen and other cations on the reactions between alkyl halides and urazole anions, and the investigation of Acree and Johnson on the reactions of carbonyl compounds with hydroxylamine and hydroxylamine salts.

The writer wishes to lay special stress on several characteristic features of the reactions between carbonyl compounds and hydroxylamine which have been met with for the first time in the study of catalytic reactions. It should be pointed out briefly that the data of Acree and Johnson seem to show that acetone and hydroxylamine in aqueous solutions unite very readily and nearly completely, as illustrated in the following expressions,

$$(CH_3)_2CO + NH_2OH \rightleftharpoons (CH_3)_2C{=}NOH + H_2O, \text{ or}$$

$$\frac{dx}{dt} = K(A - x)\,(B - x) - K'(C_{H_2O} + x)x \qquad (1),$$

[1] Lehrbuch der allgemeinen Chemie, II (2), 262. Z. Elek. Chem., 7, 995.
[2] Congress of Arts and Science, St. Louis, 1904, 4, 276.
[3] This Journal, 38, 259.
[4] See the article in this number of This Journal.

and that the velocity of the reaction is accelerated by acids because the hydroxylamine or the acetone forms cations which are much more reactive than the free bases:

$$(CH_3)_2CO + \overset{+}{N}H_3OH \rightleftharpoons (CH_3)_2C = \overset{+}{N}HOH + H_2O \quad (1'),$$

or

$$(CH_3)_2\overset{|}{C}—\overset{+}{O}H + NH_2OH \rightleftharpoons (CH_3)C = \overset{+}{N}HOH + H_2O \quad (1'').$$

As it is not known with certainty at present whether reaction (1′) or (1″) is the correct one, we shall use (1′).

The quantitative data seem to show beyond question that the *free bases*, hydroxylamine and acetoxime, as well as their *cations*, enter into the reactions. In the case of the inversion of cane sugar, hydrolysis of esters, and hydrolysis of amides by acids, however, the substance chiefly undergoing transformation is the salt or cation formed by the union of small amounts of sugar, ester, or amide with corresponding amounts of acid or hydrogen ions, as has been brought out also by Lapworth,[1] Euler,[2] Bredig,[3] Kastle,[4] Stieglitz,[5] Acree and Johnson,[6] and Goldschmidt.[7] But in the change of acylhalogenaminobenzene derivatives into halogenacetanilides in the presence of acids, the substance transformed directly is the *undissociated salt* formed by the union of the acid and acylhalogenaminobenzene. *Whether the free base, dissociated salt, or undissociated salt undergoes transformation depends simply upon the relative activity of each in the particular reaction.*

1. The noncatalyzed reaction between acetone and hydroxylamine takes place with an easily measured rapidity, and the reaction is slightly reversible. This case and Abel's are, as far as the writer knows, the first[8] in which the noncatalyzed reactions could be measured accurately. Acree and Johnson, and Acree and Nirdlinger pointed out repeatedly

[1] Mellor's "Statics and Dynamics," 1904, p. 289.
[2] Z. physiol Chem., **32**, 146. Z. physik Chem., **36**, 405, 663; **40**, 501; **47**, 356.
[3] Z. Elek. Chem., **9**, 118; **10**, 586; **11**, 528.
[4] This Journal, **19**, 894; P. Am. Assn. Adv. Sci., **47**, 238; and original paper.
[5] Congress of Arts and Science, St. Louis, 1904, **4**, 276.
[6] *Loc. cit.*
Goldschmidt and Sunde: Ber. d. Chem. Ges., **39**, 711. Goldschmidt and Udby: Z. physik. Chem., **60**, 728.
[8] Miller and Clark; J. Physic. Chem., **11**, 353.

that a characteristic feature of the catalytic changes involved in the inversion of cane sugar, hydrolysis of esters, and hydrolysis of amides, is that the *free base* and the *undissociated salt* do not enter appreciably into the reaction, and that the catalyzed reaction, involving the reactions of the cations, is, for all practical purposes, the one actually being measured.[1]

The importance of such cases as that discovered by himself, as well as by Acree and Johnson, has not been overemphasized by Abel. It is only by having all possible conceivable cases, such as a measurable noncatalyzed reaction, a measurable rapidity of formation of the intermediate products, a measurable rapidity of the reactions of the intermediate products, and similar conditions with reversible reactions, that we can be sure ultimately of the fundamental concepts concerning catalytic reactions.

2. When the amount of catalyzer (hydrogen ions) which is added is insufficient to use up all of the base, hydroxylamine and acetoxime, the noncatalyzed and the catalyzed reactions take place side by side, each with measurable rapidity. If the NH_2OH reacts with the acetone, as in (1) and (1′), the total reaction velocity would then be, in dilute solutions in which C_{H_2O} does not change appreciably,

$$\frac{d(x+x')}{dt} = K(C_{acetone} - x - x')(C_{NH_2OH} - x) - K'x + K''(C_{acetone} - x - x')(C^{+}_{NH_2OH} - x') - K'''x' \quad (2).$$

It is seen at once that the second law of catalysis[2] can not hold in such a case, nor in the rearrangement of acylhalogenaminobenzene or the reactions worked out by Abel and by Miller and Clark; *the reaction velocity cannot be proportional to the concentration of the catalyzer.*[3] Abel, however, did not

[1] Miller: J. Physic. Chem., **11**, 9.

[2] Acree and Johnson: THIS JOURNAL, **38**, 348 *et seq.*

[3] The reaction velocity and concentration of the catalyzer can be apparently proportional in two cases: (*a*) When the velocity of the noncatalyzed reaction is negligible and the catalyzer reacts completely with some constituents of the noncatalyzed reaction, as in the oxime work, where the reaction velocity is apparently proportional to the concentration of the catalyzer if there is present not more than one molecule, or ion, of the catalyzer to each one of the constituent with which it first reacts (Acree and Johnson: *Loc. cit.*, p. 350). (*b*) When the velocity of the noncatalyzed reaction and the con-

seem to see the importance of this point, which was brought out for the first time by Acree and Johnson. The only difference, aside from the reversibility of the reaction, between this case and Abel's is that the intermediate compound, $\overset{+}{N}H_3OH$ or $(CH_2)_2{=}\overset{+}{N}HOH$, is formed with immeasurable rapidity and is transformed with a measurable rapidity, whereas Abel's intermediate iodoso ion is formed with measurable rapidity and is decomposed with immeasurably high velocity.

It is at once apparent that any reaction that seems to be of a given order and furnishes definite end products may really consist of (1) many reactions having the same order and velocity and giving the same measured end products; or of (2) one chief reaction of the order and approximate velocity measured, complicated by other reactions which have very small velocity constants and which yield the same end products.

(3) Mr. L. J. Desha has found that when an alkali is added to a solution of hydroxylamine and acetone the reaction is greatly accelerated and goes practically, if not entirely, to completion. The equilibrium point produced by alkali catalyzers,

centration of the *active molecules of catalyzer-substance* (Acree, Johnson, and Nirdlinger: THIS JOURNAL, **38**, 747) are negligible, and only one molecule or ion, of the catalyzer unites with one molecule of the other substance, and one molecule, or ion, of this *catalyzer-substance* reacts with other substances present, the reaction velocity and the concentration of the catalyzer will be proportional under the mathematical conditions discussed by Acree and Johnson. When n molecules, or ions, of the catalyzer or *catalyzer-substance* enter into the chemical changes the reaction velocity is proportional to Cat^n under the conditions discussed before. Even an apparently simple reaction might become quantitatively very complicated. If one molecule each of A, B, and Cat give one molecule each of the end products C, D, and Cat, under the above conditions, then

$$\frac{dx}{dt} = K(A-x)^{\phi}(B-x)^{\varphi}Cat^{r}, \text{ when}$$

$$\phi A.rCat \underset{\text{very rapid}}{\rightleftharpoons} \phi A + rCat \text{ always holds, and}$$

$$qB + \phi A.rCat \xrightarrow[\text{very slow}]{} C + D + (\phi-1)A + (q-1)B + rCat.$$

In other words, the reaction velocity is proportional to the powers ϕ, q, and r of the concentrations of A, B, and Cat, respectively, and not to the simple concentrations. Other similar cases will be given later. This can at once be extended to reversible reactions in which the equilibrium point will change with variations in the concentrations of the reacting substances and the catalyzer, as has already been shown by Acree and Johnson, by Abel, and by Euler. As stated before, these cases in the study of catalysis will be reported later in detail.

then, is different from that produced by acid catalyzers having the same concentration. The alkali probably forms small amounts of oxyammonium anions, $\overline{NH_2O}$, which react much more rapidly with acetone than does the hydroxylamine. A stronger acid, acetoxime, is formed:

$$(CH_3)_2CO + NH_2OH + \overset{+}{K} + \overline{OH} \rightleftharpoons (CH_3)_2CO +$$

$$\overline{NH_2O} + \overset{+}{K} + H_2O \rightleftharpoons (CH_3)_2C = \overline{NO} + \overset{+}{K} + 2H_2O \quad (3).$$

It must be pointed out, however, that the acetone *may* form a salt whose anions react with the hydroxylamine.

$$(CH_3)_2CO + \overset{+}{K} + OH + \overline{NH_2OH} \rightleftharpoons (CH_3)_2C(OH)\,\overline{O} +$$

$$NH_2OH + \overset{+}{K} \rightarrow (CH_3)_2C = \overline{NO} + \overset{+}{K} + 2H_2O.$$

With three solutions, made by adding 5 cc. N potassium hydroxide, 10 cc. 0.1 N potassium hydroxide, and 3 cc. 0.1 N potassium hydroxide, respectively, to 50 cc. each of 0.1 N hydroxylamine and 0.1 N acetone, and diluting to 110 cc., the constants for the reaction at 8° were approximately 1.50, 0.30, and 0.08. The velocity constant for the noncatalyzed reaction at 8° is negligible here and in equation (2). The constant is therefore practically directly proportional to the concentration of the catalyzer.

Since the hydroxylamine, or acetone, is a very weak acid[1] and is not converted completely into anions, the above catalyzed and the noncatalyzed reactions of hydroxylamine with acetone take place side by side as discussed in section (2). Indeed, the apparently noncatalyzed reaction (1) may take place because hydroxylamine itself, as an amphoteric compound, forms anions and cations of itself or acetone, which then react with acetone or hydroxylamine:

$$NH_2OH + NH_2OH \rightleftharpoons \overset{+}{NH_3}OH + \overline{NH_2O} \quad (4).$$

This possibility will be studied experimentally.

The noncatalyzed reaction between acetone and hydroxyl-

[1] Lobry de Bruyn: Rec. Trav. Chim., **11**, 32. Hofmann and Kohlschütter: Z. anorg. Chem., **16**, 463. Bacon and Freer: THIS JOURNAL, **38**, 367.

amine takes place with measurable rapidity. Both bases and acids increase the reaction velocity very greatly[1] through the formation of intermediate anions and cations of hydroxylamine or acetone and the reaction of these ions with the acetone or hydroxylamine. This is the first catalytic reaction in a homogeneous system in which both bases and acids are known to accelerate a reversible reaction, and in which the equilibrium point varies not only with the nature of the catalyzer but also with the amount of it. Much acid produces an equilibrium in which much salt of the stronger base, hydroxylamine, is formed. When the hydrogen ions are decreased to an amount equal to those present in water, less than 10 per cent of the hydroxylamine remains. When the alkali is added, still more of the salt of the stronger acid, acetoxime, is formed, and the hydroxylamine practically disappears. Nevertheless, each one of the three reactions seems to be reversible, the equilibrium point depending upon the nature and amount of the catalyzer. The ideas discussed in sections (2) and (4) hold perfectly well for the catalysis of this reaction by bases.

These ideas make clear the fact,[2] discovered by Acree and Hinkins and by Bodenstein and Dietz, that the equilibrium point produced in the hydrolysis of esters by enzymes is different from that produced by acids. Enzymes probably accelerate such esterification and saponification reactions through the influence of the acid and basic groups in them.

It may be possible that the hydroxylamine anions and cations, $\overline{NH_2O}$ and $\overset{+}{N}H_3OH$, really accelerate the reaction between the acetone and free hydroxylamine, just as in certain other cases salts[3] bring about catalytic reactions. In any event these phenomena are exactly analogous to the increased velocity of formation of anilides from aniline and

[1] Professor Lapworth has just informed me privately that he has observed the same facts.

[2] Acree and Hinkins: THIS JOURNAL, **38**, 370. Z. Elek. Chem., **12**, 605. Dietz: Dissertation, Leipzig, 1907.

[3] Acree and Johnson: THIS JOURNAL, **38**, 259 *et seq.* Acree and Nirdlinger: *Ibid.*, **38** 489. Acree and Shadinger: *Ibid.*, **39**, 226. Arrhenius: Z. physik. Chem., **1**, 110; **4**, 226; **31**, 197. Euler: *Ibid.*, **32**, 348; Ber. d. Chem. Ges., **39**, 2726. Koelichen: Z. physik. Chem., **33**, 129.

organic acids in the presence of the halogen acid salts of aniline, and to the action of alkalis in increasing the rapidity of formation of thioureas from amines and carbon disulphide. We shall discuss these in detail in a subsequent article.

We can predict that other cases will be found in which the presence of ammonium salts causes an increase or decrease in the velocity of the action of amino derivatives on carbonyl compounds.

(4) In reversible reactions there are probably in general, though not necessarily, two substances, one in each opposing reaction, that functionate alike (as base, acid, or in tendency to form double compounds) toward the catalyzer (acids, bases, salts, enzymes, etc.), although it may not be to the same extent. In reversible reactions, in which the catalyzer forms intermediate compounds and is used up to any appreciable extent in forming the end products, an increase in the concentration of the catalyzer will disturb the equilibrium in the direction which allows the formation of more of that intermediate double compound (catalyzer-end product, $\overset{+}{N}H_3OH$, for example) which has the greatest stability. If the catalyzer is used up appreciably in salt or double-compound formation it is only when the two bases (or acids, etc.) in the opposing reactions have approximately the same affinity constants, and their salts the same dissociation constants and reaction velocities, that the equilibrium point will not be appreciably disturbed by a change in the concentration of the catalyzer. But if the catalyzer is used up to only an inappreciable extent in this formation of salt or double compound, then the equilibrium will not be disturbed appreciably if the catalyzer functionates alike in both opposing reactions.[1] The same reasoning applies to the action of enzymes, alcoholates, etc., when they act as catalyzers through the intermediate reversible formation of double compounds. The equilibrium point for the noncatalyzed reversible reaction between acetone and hydroxylamine in one gram molecule per liter concentrations is different from that of the catalyzed reversible reaction in which the concentrations of

[1] For a fuller discussion, see Acree and Johnson: THIS JOURNAL, 38, p. 352 *et seq.*

the acetone, hydroxylamine, and hydrochloric acid are also each one gram molecule per liter, and the equilibrium then varies greatly with the variation in the amount of catalyzer, hydrogen ions.[1] In other words, *the third law of catalysis does not hold in this case.*[2] This fact does not conflict with the second law of thermodynamics. It might be thought that the change in equilibrium resulting from the removal of the catalyzer could be used in doing work. But in order to remove the catalyzer the reactions which result when the catalyzer is added must be reversed, and hence the same energy must be applied in doing this as was given up in the direct reactions. That the catalyzer is really the hydrogen ion was shown by the fact that hydrochloric and hydrobromic acids in the same concentrations gave approximately the same equilibrium point. In this reversible reaction the hydroxylamine is the strong base and the acetoxime is the weak base. The greater the concentration of hydrogen ions the greater was the amount of hydroxylamine and hydroxylammonium ions found; in other words, the greater was the amount of the salt of the stronger base. But when an alkali is used as the catalyzer, more of the weak acid, hydroxylamine or acetone, is converted into the salt of the stronger acid, acetoxime. This point was worked out from a theoretical standpoint independently by Acree, Euler, and Abel, and verified by the experimental work of Acree and Johnson.

Unless all reactions are reversible, it is not impossible that a reaction which goes to completion may become a reversible reaction in the presence of a (different) catalyzer, or *vice versa*.

All of the above work makes the writer believe that *a catalyzer may influence the velocity of a reaction physically*,[3] as by condensing the reacting substances on the surfaces of solids, enzymes, etc., and hence increasing the effective con-

[1] See also Bodenstein and Dietz: Z. Elek. Chem., **12**, 605; Dietz: Dissertation Leipzig, 1907.

[2] Acree and Johnson: THIS JOURNAL, **38**, 348 *et seq.*

[3] See Bodenstein and coworkers: Z. physik. Chem., **46**, 725; **49**, 41; **53**, 166; **60**, 1. 46. Rowe: *Ibid.*, **59**, 41. Stock, Gomalka, and Heynemann: Ber. d. Chem. Ges., **40**, 532. Stock and Bodenstein: *Ibid.*, **40**, 570. Bodenstein and Dietz: Z. Elek. Chem., **12**, 605; and Dietz: Dissertation, Leipzig, 1907.

centrations, or by imparting energy to, or removing it from, the system. *A catalyzer (pure or pseudo) may change the velocity of a reaction chemically* by altering the concentration of some substance taking part in the reaction, or by forming some new substance which yields the same end products, or catalyzer-end products. In some cases certain side reactions may be developed or suppressed by the addition or removal of the catalyzer.

JOHNS HOPKINS UNIVERSITY,
Dec. 1, 1907.

l. 39
908

REVIEWS.

ELECTRONS, OR THE NATURE AND PROPERTIES OF NEGATIVE ELECTRICITY. By SIR OLIVER LODGE, F.R.S. London: George Bell & Sons. 1906. pp. 230. Price, $2.00.

This book will be welcomed for many reasons, and especially because it comes from the pen of Sir Oliver Lodge. Whatever Lodge discusses in a semipopular style is so well done that it cannot fail to attract the attention of the intelligent, even if they are not specialists.

The present book is the outgrowth of a lecture delivered before the Institution of Electrical Engineers. It "is intended throughout for students of general physics, and in places for specialists," says the author, "but most of it may be taken as an exposition of a subject of inevitable interest to all educated men."

The problems discussed in this work are among the most fundamental with which men of science are concerned, and the experimental work described, especially that of J. J. Thomson, is some of the most brilliant that has ever been carried out in the domain of physics. A glance at some of the chapter headings will show the scope of the book: Properties of an Electric Charge; Electric Inertia; Foreshadowing of the Electron; Ionization of Gases; Determination of the Mass of the Electron; Increase of Inertia Due to Very Rapid Motion; Justification for Electric Theory of Inertia; Electric and Magnetic Deflection Method for Measuring Velocity and Mass of the Particles in Compound Rays; Electric View of Matter; Further Considerations Regarding the Structure of an Atom; Summary of Other Consequences of Electron Theory; Difficulties Connected with the Electric Theory of Matter, Etc.

It will be seen from the above that the book covers just that field with which every man of science, no matter what

his special line may be, must become more or less familiar. The treatment is characteristically clear, and not so technical as to exclude it from all but the trained physicist. Any one with a good general knowledge of elementary physics can read the work, and read it with sufficient ease to enjoy it. It is fortunate that a man of the high type of Lodge does not think it an unworthy task to present such matters in a form which is accessible to the intelligent nonspecialist.

H. C. J.

LES NOUVEAUTÉS CHIMIQUES POUR 1907. NOUVEAUX APPAREILS DE RECHERCHES APPLIQUÉES À LA SCIENCE ET À L'INDUSTRIE. Par CAMILLE POULENC, DOCTEUR ES SCIENCES. Avec 196 figures intercalées dans le texte. Paris: Librarie J B. Baillière et Fils; Établissements Poulenc Frères. 1907. pp. xi+347. Price, 4 fr.

The author has followed, in this volume of the "Nouveautés Chimiques," the same general plan as in preceding years. He has collected, from the different scientific journals, brief descriptions of new forms of apparatus which are of interest to chemists. Chapter I. deals with physical, Chapter II. with purely chemical, Chapter III. with electrical, Chapter IV. with analytical, and Chapter V. with bacteriological apparatus, and the laboratory worker may well obtain useful suggestions by looking through this book.

PRACTICAL TEST-BOOK OF CHEMISTRY. By JOHN DABNEY PALMER, M.A., M.D First edition. New York: John Wiley & Sons. Price, $1.00.

This is a collection of qualitative tests for showing the presence of various chemical compounds in drugs and medicines. It is divided into "Specific Tests" and "Tests of Purity," and is intended for physicians and pharmacists. 133 pages are filled with specific tests for 162 substances; for some of these the compiler has collected a large number of tests which are given without indication of relative value or reliability; there are 23 tests for acetanilide, 37 for albumen in urine. Fifty pages are given to tests of purity of chemicals, drugs, canned vegetables, etc.

E. R.

A LABORATORY OUTLINE OF GENERAL CHEMISTRY. By ALEXANDER SMITH, Professor of Chemistry in the University of Chicago. Third edition. Revised in collaboration with WILLIAM J. HALE, Instructor in General Chemistry in the University of Michigan. New York: Century Co. 1907. pp. 136.

This is an excellent manual, and with the exception of a few experiments could be used with any text-book; to obtain the best results, however, it should be used in connection with Professor Smith's "Introduction to General Inorganic

Chemistry," to which reference is constantly made in the text. Three editions and two reprints of this manual since its appearance, in 1899, indicate that it is liked. E. R.

ELEMENTARY PRACTICAL CHEMISTRY. PART I. GENERAL CHEMISTRY. By FRANK CLOWES, D.Sc., Lond., Emeritus Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, A.R.C.Sc., Head of the Chemical Department in the Southwestern Polytechnic, Chelsea. Fifth edition. London: J. & A. Churchill; Philadelphia: P. Blakiston's Son & Co. pp. 198. Price, $1.00.

A notice of Part II. of this book appeared in THIS JOURNAL, Vol. 38, p. 251. Part I. is a handy combined text-book and laboratory manual for the use of secondary schools, in which the text-book part is condensed to brief paragraphs, liberally illustrated by laboratory experiments. A lecture course is supposed to parallel the work.

In secondary schools little time can be given to the study of science. The problem is how to use this time to best advantage. The authors offer one of the best solutions of this problem in the book reviewed, giving nearly all the time to laboratory experiment, which is just the training the pupil needs. E. R.

BEET SUGAR MANUFACTURE AND REFINING. Vol. II: Evaporation, Graining and Factory Control. By LEWIS S. WARE. New York: John Wiley & Sons. 1907. Price, $5.00.

This volume completes the most comprehensive treatise on beet sugar manufacture in the English language. Its forty and odd chapters are grouped under the following headings: Evaporation, Manufacture of Raw Sugar, Working Afterproducts, Manufacture of White Sugar, Utilizaton of Residues, Steam Economy, and Practical Work of a Beet Sugar Factory. To this are added numerous tables, largely of Claassen's compilation, and a fair index. The second volume follows the plan of the first, being a well arranged selection of the best foreign literature. It is very well illustrated and gives copious references to the original authorities.

The reviewer regrets that he is again obliged to call attention to the poor English and unsatisfactory translation evident in many places, and especially deplorable in a work of such importance and general excellence in most details of text and typography.

"Tramp" appears in several places for "trap;" "schema," which has a quite different meaning in English, is used for "scheme" (diagram). It is doubtful whether the average technical man would know what is meant by the French "ruissellment," albeit "rendement" and "entrainment" are

well-recognized terms in the industry. Much worse is the use of "sheet iron" for "boiler iron."

Perhaps the most glaring instance of all is the table on p. 639, apparently translated from the German of Claassen. Statements such as "cast iron tube, riveted and enameled," "soldered, forged-iron boiler tube," etc., are not only mistranslated and badly rendered but are senseless to the engineer.

Other cases, such as "mushrooms" for "fungi," could be cited. The reviewer knows too well, from his own experience, how easily such slips are made, especially in translations; still it is regrettable that the editing could not have been better in a work of this importance. It is hoped that such blemishes can be removed in a later edition. GEO. W. ROLFE.

TENTH ANNUAL CONVENTION OF ASSOCIATION OF STATE AND NATIONAL FOOD AND DAIRY DEPARTMENTS. New York: John Wiley & Sons. 1906. pp. vi + 349. Price, $3.00.

This publication is of unusual interest in connection with the literature of food legislation and of the manufacture and sale of foods. The proceedings are given in full and include reports and discussions of representatives of the federal and state officers charged with the enforcement of food laws, as well as addresses of manufacturers and dealers in foods. Aside from a record of the resolutions adopted by the Association and the reports of committees, the publication contains the full text of twenty-two addresses on miscellaneous food topics and on the federal food laws and the regulations adopted for their enforcement. The publication is well arranged and has a comprehensive general index. W. D. BIGELOW.

CHEMICAL REAGENTS. THEIR PURITY AND TESTS. A New and Improved Text Based on and Replacing the Latest Edition of Krauch's "Die Prüfung dea chemischen Reagentien auf Reinheit." By E. MERCK. Authorized translation by Henry Schenk, A.B. (Harvard). New York: D. Van Nostrand Co. 1907. 250 pp. Price, $1.50.

This volume gives the characteristics and constants of more than six hundred chemical reagents with well-chosen tests of purity for each.

The former editions of Dr. Krauch's work were well received, and the present translation of the enlarged and revised edition should be within reach of every working chemist. E. R.

GLUES AND GELATINE. A PRACTICAL TREATISE ON THE METHODS OF TESTING AND USE. BY R. LIVINGSTON FERNBACH.

Referring to a review of the book bearing the above title which appeared in the September number of this Journal, the Editor desires to say that the article was in no sense an expression of his own personal views, and that he is not in a position to pass upon the merits of the work. So far as the article in question may have appeared to be unduly harsh, the Editor hereby expresses his regret.